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<u>L7</u>	koch same membrane and nanofiltration	36	<u>L7</u>
<u>L6</u>	L5 and koch	2	<u>L6</u>
<u>L5</u>	sr1 and membrane	197	<u>L5</u>
<u>L4</u>	membrane and sr and nanofiltration	25	<u>L4</u>
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<u>L1</u>	tfc and membrane	102	<u>L1</u>

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PALM INTRANET

Continuity Information for 10/374901

Parent Data

No Parent Data

Child Data

PCT/US04/05408 is a continuation of 10374901

Appln Info

Contents

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Atty/Agent Info

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L3: Entry 2 of 2

File: USPT

May 12, 1992

DOCUMENT-IDENTIFIER: US 5112483 A

TITLE: Slow sand/nanofiltration water treatment system

Brief Summary Text (5):

The prefix nano means one thousand millionth or 10^{-9} . One nanometer is equivalent to 10 angstroms. The NF-70 NANOFILTRATION membranes made by FilmTec, a subsidiary of Dow Chemical Company, will reject all molecular species of 10 angstroms or greater in diameter consistent with a 200 molecular weight cutoff. Rejection of molecular species below a 200 molecular weight is dependent on their size, ionic charge and membrane affinity. This molecular weight cutoff is ideal for eliminating organic precursors that are not removed in conventional water treatment plants. These nanofilters will remove most of the sulfate, calcium and magnesium products in the water and about 1/2 of the sodium and chloride compounds. Other companies, including Desal, make a similar type of membrane.

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L4: Entry 5 of 11

File: USPT

Oct 15, 2002

DOCUMENT-IDENTIFIER: US 6464873 B1

TITLE: Interfacially polymerized, bipiperidine-polyamide membranes for reverse osmosis and/or nanofiltration and process for making the same

Brief Summary Text (3):

It is known that dissolved substances can be separated from their solvents by the use of semi-permeable membranes. For example, of great practical interest is the removal of salts from water by reverse osmosis (RO) or by nanofiltration (NF). The efficiency and economy of such removal is of tremendous economic significance in order to provide potable water from brackish or sea water for household or agricultural use. A critical factor in desalination is the performance of the membrane in terms of salt rejection, i.e., the reduction in salt concentration across the membrane, and flux, i.e., the flow rate across the membrane. For practical RO applications, the flux should be on the order of greater than at least 15 gfd ("gallons per square foot per day") at a pressure of about 15 atmospheres for brackish water. More preferably, commercial RO applications now require fluxes greater than about 25 gfd (about 1.0 m.sup.3/ m.sup.2 -day) at a pressure of about 15 atmospheres for brackish water. NF applications require at least 30 gfd (about 1.2/m.sup.3 m.sup.2 -day) at a pressure of 10 atmospheres. Moreover, salt rejections greater than 99% are required for RO and greater than 50% for NF. The continuing goal of research and development in this area is to develop membranes having increased flux and/or solute rejection, which are useful in desalination and removal of other low molecular weight solutes.

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☐ 1. Document ID: US 6645383 B1

L7: Entry 1 of 3

File: USPT

Nov 11, 2003

US-PAT-NO: 6645383

DOCUMENT-IDENTIFIER: US 6645383 B1

TITLE: Process and apparatus for blending product liquid from different TFC membranes

DATE-ISSUED: November 11, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Lee; Barry H.	Des Plaines	IL		
Wayman; Gene	Fox River Grove	IL		
Van Newenhizen; John	Mundelein	IL		

US-CL-CURRENT: 210/652; 210/257.2, 210/641, 210/653

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KUOC	Draw D
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☐ 2. Document ID: US 5868937 A

L7: Entry 2 of 3

File: USPT

Feb 9, 1999

US-PAT-NO: 5868937

DOCUMENT-IDENTIFIER: US 5868937 A

TITLE: Process and system for recycling and reusing gray water

DATE-ISSUED: February 9, 1999

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Back; Dwight Douglas	Melbourne	FL		
Scaringe; Robert Peter	Rockledge	FL		
Ramos; Charlie	Satellite Beach	FL		
Samad; Nidal Abdul	Palm Bay	FL		
Gann, Sr.; Steven Dale	Merritt Island	FL		

US-CL-CURRENT: 210/651; 210/167, 210/195.2, 210/257.2, 210/650, 210/805, 210/98

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KMIC	Draw D
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3. Document ID: US 5607593 A

L7: Entry 3 of 3

File: USPT

Mar 4, 1997

US-PAT-NO: 5607593

DOCUMENT-IDENTIFIER: US 5607593 A

**** See image for Certificate of Correction ****

TITLE: Installation for making water potable with submerged filtering membranes

DATE-ISSUED: March 4, 1997

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Cote; Pierre	Maisons-Laffitte			FR
Faivre; Michel	Acheres			FR
Moulin; Catherine	Paris			FR
Desbos; Gilbert	Maisons-Laffitte			FR

US-CL-CURRENT: 210/650; 210/195.2, 210/220, 210/257.2, 210/258, 210/321.69,
210/323.2, 210/333.01, 210/333.1, 210/636, 210/651, 210/652, 210/758, 210/760

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KMIC	Draw D
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<u>L4</u>	potable water same nanofiltration	11	<u>L4</u>
<u>L3</u>	nf-70 same nanofiltration same charge	2	<u>L3</u>
<u>L2</u>	L1 and positively charge same nanofiltration	0	<u>L2</u>
<u>L1</u>	nanofiltration and membrane and positively charged	33	<u>L1</u>

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L11: Entry 1 of 2

File: USPT

Sep 19, 2000

DOCUMENT-IDENTIFIER: US 6120689 A

TITLE: High purity water using triple pass reverse osmosis (TPRO)

Brief Summary Text (3):

In producing a high purity water product using reverse osmosis membranes, it is difficult to reject gases such as carbon dioxide and/or ammonia. The carbon dioxide and ammonia gas pass through the reverse osmosis system and re-establish an equilibrium in the product water. This, of course, adversely affects the product water quality, e.g., resistivity.

Brief Summary Text (4):

Many processes have been suggested to provide high purity water. For example, U.S. Pat. No. 5,178,766 suggests the use of a composite semipermeable membrane comprising a microporous substrate; and a cross-linked polyamide-based ultra-thin membrane superposed on the microporous substrate, the ultra-thin membrane having covalently bonded quaternary nitrogen atoms. When such a membrane, i.e., cross-linked polyamide-based composite semipermeable membrane, is used, it is suggested that a double pass reverse osmosis system is sufficient to produce high purity water. That is, a regenerative ion-exchanger normally used may be eliminated.

Brief Summary Text (5):

U.S. Pat. No. 5,670,053 discloses a process for purifying water including removing cations, anions and carbon dioxide and/or ammonia from water feed stream to produce high purity water having a resistivity of greater than 1 megohm-cm comprising the steps of providing a water feed stream to be purified. In this system, a gas permeable hydrophobic membrane is provided between a first reverse osmosis system and a second reverse osmosis system for removing carbon dioxide and/or ammonia gas through a gas permeable hydrophobic membrane.

Brief Summary Text (6):

U.S. Pat. No. 5,061,374 discloses an improved deionized water treatment system and method that consists of using a first and second water treatment train wherein the second train improves water quality by reducing particulate and total organic carbon by means of a reverse osmosis membrane assembly. The final pure water has particulate sizes less than one micron and a total organic carbon measure of less than one part per billion.

Brief Summary Text (8):

U.S. Pat. No. 4,980,066 discloses an improved membrane separation system which comprises a plurality of discrete membrane separation units, each membrane separation unit comprising at least two membranes and also comprising an inlet for process fluid and optionally an outlet for process fluid. Each membrane separation unit is located within a container for permeate, the container comprising a permeate outlet and wherein the container is such as to enable the membrane separation units to be at least partially immersed in permeate.

Brief Summary Text (9):

U.S. Pat. No. 5,651,894 discloses an ultrapure water purification scheme that incorporates the use of certain reverse osmosis filtration membranes that are especially susceptible to oxidative attack. The scheme employs the combination

reducing/metals scavenger/biocidal agent dithiocarbamate as a pretreatment additive to maintain a nonoxidizing environment, to bind contaminant metals to improve their removal from source water, and to reduce microbial content. In addition, the generation of oxidants by cavitation effects is avoided by a reduced pressure retentate recycle. Both measures prevent oxidative attack and fouling of the reverse osmosis membranes.

Brief Summary Text (10):

U.S. Pat. No. 5,128,041 discloses microporous membranes having positive zeta potentials in alkaline pH which are provided by radiation grafting diallyldimethylammonium dimethyl ammonium chloride to the surfaces of a microporous, polyamide membrane using ionizing radiation. The membranes have particular use in microelectronics manufacture where quick rise up times with ultrapure water are required.

Brief Summary Text (11):

Thus, it will be seen that there is a great need for a process which can be tuned to the system, including feedwater and the use of different membranes, and which will consistently produce high resistivity water on a continuous basis, even with changing composition of the feedwater.

Brief Summary Text (16):

It is yet another object of this invention to provide an improved process employing three reverse osmosis membranes having a combination of charged and non-charged membranes.

Brief Summary Text (17):

It is yet another object of this invention to provide a system employing three reverse osmosis membranes for producing high quality water with low concentrations of weakly acidic anions, such as silicates and borates.

Brief Summary Text (18):

And it is yet another object of this invention to provide a system employing three reverse osmosis membranes capable of producing high purity water having a resistivity in the range of 10 to 18 megohm-cm.

Brief Summary Text (19):

Yet, it is another object of this invention to provide an improved process employing three reverse osmosis membranes for producing high purity water by utilizing product water resistivity to control pH of feedwater or interpass water in the system.

Brief Summary Text (23):

In accordance with these objects, there is provided a method for producing high purity product water using a three pass reverse osmosis system, the method having the ability to produce water having a resistivity in the range of 10 to 18 megohm-cm. The method comprises the steps of providing a feedwater to be purified, the feedwater preferably having a basic pH. The feedwater is introduced to a high pressure side of a first reverse osmosis membrane module preferably comprising a non-charged membrane, and water is passed through the first reverse osmosis membrane to provide a first retentate and a first permeate, the first permeate maintained at a basic pH. The first permeate is transferred to a high pressure side of a second reverse osmosis membrane module and is further purified by passing at least a portion thereof through the second reverse osmosis membrane to provide a second retentate and a second permeate having a pH of less than 6.2 and resistivity in the range of 0.5 to 2.5 megohm-cm. The second permeate is adjusted to a pH in the range of 6.2 to 8.5 to provide an adjusted second permeate. A third pass reverse osmosis module is provided having a third high pressure side and a third low pressure side, the third pass reverse osmosis module preferably comprising a third pass reverse osmosis membrane selected from a positively charged membrane and

a negatively charged membrane. The adjusted second permeate is introduced to the high pressure side of the third pass reverse osmosis module and at least a portion of said adjusted second permeate is passed through said third pass reverse osmosis membrane to permeate high purity product water having a pH in the range of 6.8 to 7.2.

Drawing Description Text (4):

FIG. 3 is a schematic illustrating that different pH values can produce equivalent resistivity product water from different membranes, and that product resistivity is a function of feed pH and low alkalinity low TDS (total dissolved solids) feed.

Detailed Description Text (5):

It should be noted that different combinations of membranes can be used in the triple pass reverse osmosis systems of the present invention, depending to some extent on the materials desired to be removed at each step. Further, improved quality of water is obtained if membranes are selected for each pass whose operating characteristics, such as salt rejection at high and low pH, optimum and allowable range of operating pH, are matched to the removal of material desired in each pass, and the actual dissolved materials in each pass. This is particularly important in the third pass at low feed TDS. In one embodiment of the invention, the membranes selected for membrane modules 10 and 18 are preferably spirally wound, negatively charged low pressure, interfacially cast fully aromatic, polyamide membranes, while membrane selected for module 28, although also of polyamide and interfacially cast, is preferably a positively charged membrane. The negative and positive charges on these membranes are derived from carboxyl and amine groups, respectively. Negatively charged membranes are available from Fluid Systems Corporation, under the designation HRRX, and positively charged membranes from Toray Industries Inc., under the trademark Romembra.RTM. and designation SU900.

Detailed Description Text (6):

The triple pass reverse osmosis system, however, may be configured using a wide variety of membrane configurations and chemistries. Other membrane configurations may be used, such as hollow fiber, with inside-out or outside-in flow, plate and frame or tubular. Other chemistries which may be used in one or more passes include neutral and asymmetric membranes, such as cellulose acetate, cellulose triacetate, and cellulosic blends. Other neutral polymers that may be used include strongly and weakly charged membranes other than polyamides. Cellulose acetate blend membranes are available from Fluid Systems Inc. under the trademark ROGA.RTM., having the designation 4221 FR. An example of an interfacially cast membrane based on polysulfonated polyethersulfone is made by Acumem, Inc. under the trademark Acumem.RTM. DPOU.

Detailed Description Text (7):

Cellulose acetate membranes are somewhat restricted in their use due to a limited range of pH, with a maximum recommended operating pH of 6.0, and preferably 5.7. At higher pH, membrane hydrolysis will be accelerated. When a cellulose acetate membrane is used in first pass service, pH in the first pass may range from 5 to 6. Other neutral membranes can also be used in the final pass; however, such membranes must be inert to water at about pH 7. Membranes with neutral chemistries are preferred for the third pass because such a membrane will give balanced rejection of fixed anions and cations. Negatively and positively charged membranes may be used in the third pass but will preferentially reject fixed anions and cations, respectively.

Detailed Description Text (8):

Negatively charged membranes preferentially reject fixed anions (e.g., Cl.sup.- and SO₄.sup.=.sub.4) in the feedwater, while positively charged membranes preferably reject fixed cations (such as Na.sup.+ and Ca.sup.++). However, the differences in rejection for ions of the same valence and hydrated ionic radius is usually small,

by comparison with overall rejection. Furthermore, such differences may not be significant, for product water end uses in which the major quality requirement is high resistivity. The important requirement for third pass service is good rejection, at low TDS levels, of those monovalent species (Na^+ , K^+ , Cl^-), which are most abundant in third pass feedwater, and of bicarbonate/carbonate species, if present. Rejection of weakly acidic anions, such as silicates, is desirable but not essential, since these species can also be rejected in the preceding passes, using different membranes and operating conditions.

Detailed Description Text (9):

In one embodiment of the present invention, the first and second membranes can be neutral (no charge) membranes followed by a third membrane either positively or negatively charged, depending to some extent on the water being purified.

Detailed Description Text (10):

When a neutral membrane is used which is resistant to acid or base material, the pH to the first pass can range from 4.5 to 10.5.

Detailed Description Text (11):

The first permeate is used as feed for second reverse osmosis 18. The purpose of first and second reverse osmosis systems is to reduce the alkalinity and TDS to a low level. The second permeate produced at low pressure side 22 preferably has a pH of less than 6.2, an alkalinity of less than 0.2 mg/l expressed in terms of CaCO_3 and a resistivity in the range of 0.5 to 2.5 megohm-cm. Further, preferably, gases which dissolve to form acidic or basic ionized species should be essentially absent in free form in the feed to the third pass because such gases otherwise pass freely through the third membrane and adversely affect product resistivity. If such gases are present, they can be removed by any suitable means such as pH change or by a high efficiency degassing step. These conditions are important in order to consistently produce a high purity water product from third reverse osmosis 28, for example, having a resistivity in the range of 10 to 18 megohm-cm.

Detailed Description Text (12):

As noted earlier, the permeate from second reverse osmosis 18 is directed to third reverse osmosis 28. In the present invention, regardless of the membranes used in the first and second reverse osmosis modules, for example, two neutral membranes, it is preferred that third reverse osmosis membrane in module 28 be selected from a positively charged membrane and a negatively charged membrane. The third membrane can also be neutral, but cellulose acetate only produces a product water typically having a resistivity of less than 10 megohm-cm. When a positively or negatively charged membrane is used in the third reverse osmosis unit, the pH of the second permeate is adjusted upwardly to a pH in the range of 6.2 to 8.5 to provide an adjusted second permeate for use as a feed to the third reverse osmosis unit. When the third reverse osmosis unit utilizes a positively charged membrane, then the pH of the second permeate is adjusted to a pH in the range of 7 to 8.5, preferably 7.5 to 8.5 to ionize remaining carbon dioxide gas to produce bicarbonate ion (HCO_3^-) which is efficiently rejected by the positively charged membranes. The pH of the second permeate can be adjusted using any hydroxide material; however, sodium hydroxide is preferred. An electrolytic half-cell may also be used. This has the advantage that no additional fixed anion or cation is introduced when a half-cell is used to adjust the pH upwardly or downwardly. This process can efficiently produce high purity product water having a resistivity in the range of 10 to 18 megohm-cm and a pH in the range of 6.8 to 7.2, typically at a pH of about 7. Positively charged membranes suitable in this invention are described in U.S. Pat. No. 5,178,766, incorporated herein by reference.

Detailed Description Text (13):

If neutral membranes are used in the first and second pass along with a negatively

charged membrane in the third pass, then it is preferred to subject the second permeate to additional treatment steps prior to introducing it to the third reverse osmosis unit. That is, the second permeate is treated to lower the pH to a pH of less than about 4.5 to provide an acidic solution having molecular carbon dioxide. The acidic solution is then subjected to a degassing step to remove the carbon dioxide to provide a degassed liquid. The degassing may be performed as described herein with respect to FIG. 2, for example. In the degassing step, it is important to reduce the carbon dioxide to a very low level, for example, less than 500 parts per billion (ppb). After the degassing step, the pH of the second permeate is adjusted to a pH of at least 6.5, preferably to a pH in the range of 7 to 8.5. The pH may be adjusted by adding sodium hydroxide. After degassing and pH adjustment, the second permeate is introduced to high pressure side 26 of third reverse osmosis unit 28 and high purity water is permeated through a negatively charged membrane into low pressure side 38. This system is capable of producing high purity water having a resistivity in the range of 10 to 18 megohm-cm. Typically, the pH of the high purity product water is in the range of 6.8 to 7.2 typically at a pH of about 7. The negatively charged membrane is particularly effective in rejecting negatively charged ions, e.g., monovalent negatively charged ions such as chloride and bicarbonate remaining in the second permeate.

Detailed Description Text (14):

In the present invention, when negatively charged membranes are used in the first and second passes, the feedwater pH can range from 8 to 11. The higher pH is particularly effective in removing silica. Further, it is preferred to maintain the first permeate at a pH in the range of 6.5 to 7.8. Also, the feedwater may be subjected to softening treatments as described herein to minimize scaling.

Detailed Description Text (15):

In another aspect of the invention, the feedwater to first reverse osmosis unit 10 may be adjusted to a pH in the range of 8.3 to 11 for purposes of ionizing weakly acidic material such as ionized forms of silica and boron which have high pKa's. The first pass typically removes substantially all strongly ionized divalent anions, such as sulphate, nitrate and cations such as calcium, barium and strontium ions, if present and most monovalent ions, such as sodium and chloride. Carbonate and bicarbonate removal is enhanced as the pH is raised. The higher pH is particularly useful in removing silica. A portion of the feedwater is passed through the membrane in reverse osmosis unit 10 and recovered as a first permeate having a pH in the range of 7 to 10, preferably 7.5 to 9.5. This first permeate is passed through second reverse osmosis unit 18 which removes additional smaller ions such as sodium and chloride. Additional bicarbonate as well as other ions are removed to provide a second permeate having a pH of less than about 6.2 and a resistivity in the range of 0.5 to 2.5 megohm-cm.

Detailed Description Text (17):

feedwater and the first permeate basic, the first and second membranes are effective in removing substantially all of the TDS and alkalinity. For example, by maintaining an alkaline pH substantially all of the TIC (total inorganic carbon) is fixed as CO₂, which is effectively removed. Further, removal of weakly ionized material is enhanced at an alkaline pH.

Detailed Description Text (18):

In this particular aspect of the invention, the membranes employed in reverse osmosis units 10 and 18 are preferably negatively charged membranes and the membrane employed in module 28 is preferably a positively charged membrane. As noted, such negatively charged membranes are available from Fluid Systems Inc. under the designation HRRX and the positively charged membrane is available from Toray Industries Inc. under the designation SU900.

Detailed Description Text (19):

In this particular aspect of the invention, it is preferred to subject the

feedwater to an ion exchange softening step to remove scaling cations such as calcium, strontium and barium. Alternatively, the feedwater can first be subjected to nanofiltration. In addition, TDS including sodium can also be removed, depending on the membrane used and the composition of the feedwater. The second permeate is adjusted to a pH in the range of 6.2 to 8.5 before passing a portion thereof through a third reverse osmosis to provide high purity water. The membrane suitable for use in the third reverse osmosis unit may be a positively or negatively charged membrane. If a positively charged membrane is used, the pH can be adjusted to about 7.5 to 8.5. If a negatively charged membrane is used, the second permeate is acidified to a pH of less than 4.5 and degassed to remove carbon dioxide, as noted, before adjusting to a pH greater than 6.2, preferably 6.5 to 8.5, before passing through the third reverse osmosis.

Detailed Description Text (20):

In a further aspect of the invention, the feedwater to first unit 10 is adjusted to an acidic pH, preferably a pH in the range of 5 to 7 and typically 5.5 to 6.5 for purposes of rejecting ionizing materials such as ammonia and to prevent scaling resulting from calcium carbonate. The acidic pH also reduces total alkalinity by reactions that form carbon dioxide and fixed anions such as chloride and sulfate, depending on the acid used. The membrane utilized in reverse osmosis module 10 can be any membrane; however, it is preferred to use a neutral membrane or a negatively charged membrane as described herein to minimize fouling resulting from organic matter. The first pass membrane removes a significant portion of the feedwater TDS, and substantially all of the alkalinity while at the same time permitting free carbon dioxide to pass with the first pass permeate. The permeate from first reverse osmosis unit 8 is maintained in an acidic condition, and preferably maintained at a pH of less than 6 and typically at a pH in the range of 4 to 6, e.g., 5.5. The acidic pH, e.g., 5.5, provides carbon dioxide in a molecular or gaseous form which can be removed by degassing as described herein. Thus, the first permeate is subjected to a degassing step which will result in an increase in pH.

Detailed Description Text (21):

Thereafter, the degassed permeate is subject to a second reverse osmosis treatment in reverse osmosis unit 18. The degassed feed to reverse osmosis unit 18 typically has a pH in the range of 6.5 to 7 which permits removal of substantially all of the remaining alkalinity. Preferably, the membrane used in reverse osmosis unit 18 is a negatively charged membrane. Treatment in reverse osmosis unit 18 provides a second permeate having a pH of less than 6.2, preferably less than 6, and a resistivity in the range of 0.5 to 2.5 megohm-cm. The second permeate is adjusted to a pH of greater than 6.2, e.g., 6.2 to 8.5 before being used as feed to the high pressure side of third reverse osmosis module 28. The third permeate emanating from the third reverse osmosis unit provides high purity water in accordance with the invention, typically having a pH in the range of 6.8 to 7.2. Preferably, the membrane for the third reverse osmosis is either a positively or a negatively charged membrane as described herein. The feedwater used for this application wherein the feed to the first and second reverse osmosis units is maintained acidic, may be subjected to any of the water softening treatments described herein.

Detailed Description Text (22):

The presence of total alkalinity due mainly to bicarbonate, smaller amounts of carbonate and of carbon dioxide with small contributions by other ions in the feedwater is responsible for significant changes in apparent rejection of salts as determined by the conductivity of product water from a reverse osmosis system. As noted, reverse osmosis membranes are transparent to dissolved gases. Thus, carbon dioxide present in the feed side of the first pass membrane passes through the membrane to the interpass while bicarbonate and carbonate comprising total alkalinity is mostly rejected along with other anions and cations. This results in a change in the total alkalinity:CO₂ ratio, a loss of buffering capacity and causes a drop in pH from feed to interpass or permeate from the first membrane in a

double pass reverse osmosis system. The same process is repeated from the interpass to the second pass product, for example. The resulting change in the interpass pH can have the result of moving the interpass pH away from the pH which results in high resistivity product water from the second pass reverse osmosis unit. Thus, setting the pH of the feedwater to a multi-pass reverse osmosis system does not always result in high resistivity product water.

Detailed Description Text (23):

In addition, when a particular pH is chosen for producing high resistivity water from a particular feedwater, changes in the feedwater composition, e.g., alkalinity, can render the chosen pH not optimum. Thus, lower quality product water results even though the feedwater has been maintained within a narrow pH range which was, at one time, thought to be optimum. Further, it will be appreciated that different membranes have the capacity to reject different ions to a lesser or greater extent. That is, some membranes reject fixed anions better than cations and vice versa. When there is preferential rejection, there can be leakage of the other or opposite ion. At low TDS, pH of the feedwater has a large impact on the capacity of the particular membrane to reject the particular anion or cation. However, any charged membrane's performance can vary in a systematic way with pH to reach a peak value for rejection, and thereafter its performance declines on either side of an optimum pH.

Detailed Description Text (24):

This concept is illustrated in FIG. 3 where A and B denote the highest resistivity for a given pH value. However, on either side of the peak resistivity value, resistivity declines with rising or falling pH. FIG. 3 also illustrates that different pH values can result in the same quality product water. However, on either side of the pH value, product quality declines. A can represent first pass feed pH for low alkalinity/low TDS feedwater and B can represent first pass feedwater pH for higher alkalinity/TDS. A can also represent the optimum pH for a typical negatively charged conventional polyamide membrane, whilst B represents the optimum for another type of membrane. The negatively charged membrane of Fluid Systems Inc., referred to by the tradename HRRX membrane, operates in a pH range of 6.5 to 8 with a 99.4% rejection, while Toray's positively charged membrane, having the designation SU910S, operates at a pH of 9 to 9.5 with a 99.5% rejection. The lower pH is better for removing ammonia and the higher pH is better for removing carbon dioxide.

Detailed Description Text (32):

Because of the presence of scale forming cations, such as magnesium and calcium, membrane scaling can occur in the primary reverse osmosis module 10. Thus, for purposes of the invention, it is preferred to pretreat the feedwater to remove the scale forming cations. Conventionally, such pretreatments include water softening. However, this has the disadvantage that large quantities of salt are required for regeneration of the softener. Thus, for purposes of the present invention, pretreatment of the feedwater utilizing a softening or nanofiltration membrane is also acceptable. The nanofiltration membrane operates at about 1/4 to 1/3 the pressure (e.g., 60 to 120 psig) required for a reverse osmosis membrane used for purifying brackish water. Thus, nanofiltration can be used for pretreatment of the feedwater to remove scale forming precipitates, colloidal and organic material which would operate to foul the primary reverse osmosis membrane. The nanofiltration membrane is effective in removing up to about 80% of the large ionic radius ions and radicals, such as calcium, magnesium, sulfate and to a lesser extent, bicarbonate. Sodium and chloride ions, because of their small ionic radius, are not effectively removed (about 20 to 40% by nanofiltration). Thus, if caustic is used to adjust the pH of the feedwater, water softening or nanofiltration should be used to remove multivalent cations. The use of nanofiltration as a pretreatment has the advantage over conventional softening of not requiring the use of large quantities of regenerant salt or the disposal of regenerant waste solutions. Further, the use of nanofiltration as a pretreatment has the advantage that fouled

nanofiltration membranes are much easier to clean when compared to conventional reverse osmosis membranes.

Detailed Description Text (33):

Nanofiltration membranes useful in the present invention are available from Filmtec, A division of Dow Chemical Company under the designation NF-40 or NF-70. Typically, nanofiltration membranes useful in the invention have a pore size in the range of 0.005 to 0.05 μm , and preferably 0.008 to 0.02 μm . In the present invention, nanofiltration is preferred for pretreatment of feedwater having a total dissolved solids of 200 ppm or greater and high percent hardness, e.g., 75% or greater, due to cations such as calcium and magnesium ions. The nanofiltration operates to remove 50 to 80% of the scale-forming precipitates. Thus, nanofiltration operates to reduce both alkalinity or dealkalize the feedwater and to reduce total dissolved solids from the feedwater.

Detailed Description Text (37):

In another method of removing chloramine, sodium bisulfite may be added to the feedwater for purposes of removing chlorine. That is, sodium bisulfite acts to break down chloramine to chloride and ammonia gas. The chloride ion is rejected by the reverse osmosis membrane. The ammonia gas becomes ionized in the pH range below 7 and will be rejected by the reverse osmosis membrane. Thus, in some instances it is preferred that at least one interpass permeate be maintained at a pH in the range below 7 in order that the reverse osmosis unit 18 can remove the ammonium ion. The interpass permeate can be maintained at a lower pH, e.g., 6 to 7, by selecting a first pass membrane (reverse osmosis unit 10) that has a high salt rejection which operates to reduce alkalinity to a greater extent in the first pass while still allowing passage of carbon dioxide. This results in a lower pH for the interpass permeate. Also, if the feedwater is partially dealkalized, the pH of the feedwater entering reverse osmosis unit 10 can be lower resulting, in some instances, in a lower pH for the interpass permeate.

Detailed Description Text (40):

The dealkalized feedwater is conveyed along line 70 to degassing station or unit 72 for removing carbon dioxide. The feedwater is degassed by providing a vacuum on one side of a microporous, hydrophobic membrane such as is available from Hoechst-Celanese Corp. under the trademark Liqui-Cel.RTM.. The degassing may be accomplished using a vacuum and a gas purge of nitrogen or by an air sweep at atmospheric pressure. In degassing unit 72, 80% and preferably 90% of the free carbon dioxide is removed. The vacuum is obtained by blowing air, using blower 74, through line 76. The air exits along line 78. Degassed feedwater is removed along line 80 to water softener 82. The pH of the feedwater can be lowered prior to its entering degassing unit 72 to favor removal of carbon dioxide gas. pH of feedwater in the range of 8 to 10 is useful for the present invention.

Detailed Description Text (43):

In the present invention, alkalinity in the feedwater resulting from bicarbonate, carbonate and minor amounts of other ions as well as carbon dioxide significantly affect rejection of salts and thus the level of conductivity or resistivity of the product water from a triple pass reverse osmosis system. The presence of alkalinity and carbon dioxide result in poorer quality product water than would normally be predicted from rejection of sodium chloride only. Dissolved gases such as carbon dioxide pass through a reverse osmosis membrane while most of the alkaline material is rejected. This causes a drop in the pH of permeate from the first reverse osmosis by changing the alkalinity:carbon dioxide ratio. Thus, it will be seen that such change in pH in respect of interpass permeate may not be optimum for production of product water having a high resistivity. However, by monitoring product water resistivity in accordance with the invention, the feedwater can be adjusted to provide a feed or an interpass permeate having a pH in the range of 6 to 7.5 which permits production of product water having high resistivity. That is, at a pH in the range of 6 to 7, any ammonia gas becomes ionized and is easily

rejected in reverse osmosis unit 18. Thus, it is preferred to adjust the pH of the interpass permeate by adjusting the alkalinity of the feedwater. The interpass permeate can be degassed or treated with acid to ionize ammonia gas for rejection in the next pass. The interpass permeate pH can be adjusted also with alkali or base material, buffer, a natural or synthetic material such as resin or zeolite, an electro or electrochemical ion exchange process. Also, the interpass permeate can be degassed using a hydrophobic membrane where a vacuum is provided on one side to remove gases through the membrane.

Detailed Description Text (47):

After the pH of the pretreated feedwater is adjusted, it is introduced to high pressure side 8 of reverse osmosis 10 where ionized material, such as sodium, chloride, sulfate, bicarbonate and silica, as well as other ions, are rejected and removed along line 10. As noted earlier, the alkalinity:carbon dioxide ratio is changed in reverse osmosis 10, and this causes a drop in pH for the interpass permeate. Thus, it is important that the pH of the interpass permeate is changed in the direction desired for optimum resistivity of product water. When the pH of the feed to a particular reverse osmosis unit is matched with the membrane used, this provides for the production of high purity water. Thus, in such cases, addition can be made to the interpasses to adjust the feed to the desired pH level for rejection by the membrane.

Detailed Description Text (48):

Suitable membranes that can be utilized in reverse osmosis units 10 and 18 are available from Fluid Systems Inc. under the designation HRRX.

Detailed Description Text (57):

Tap water was purified continuously in a triple pass reverse osmosis system substantially as shown in FIG. 1. The feedwater had a conductivity of 300 micro-S-cm, a total alkalinity (as CaCO.sub.3) of 89, and a pH of 7.9 with a total hardness (as CaCO.sub.3) of 92 mg/l. The tap water feed was pretreated by softening, dechlorinated by passing through granular activated carbon, and subjected to a 5 micron cartridge filtration step, prior to adjusting to a pH of 8.1. The reverse osmosis unit utilized negatively charged polyamide, spirally wound elements. The recirculating feed to the first reverse osmosis unit had a conductivity of 450 micro-S-cm, total alkalinity (as CaCO.sub.3) of about 140 mg/l and a total hardness of <1 mg/l after stabilized flow was established. First pass permeate pH was in the range of 7.5-8.0. The first pass permeate was used as feed to the second reverse osmosis unit, which also utilized negatively charged polyamide, spirally wound elements. After passing through the second reverse osmosis unit, the second permeate had a conductivity of 0.5 to 2 megohm-cm, a pH of about 6.2, and an alkalinity level of <1 mg/l (as CaCO.sub.3). The second permeate was directed to a third reverse osmosis unit, which used a positively charged membrane. The membrane was operated at a recovery of 50% at 25.degree. C. It will be seen from FIG. 4 that the best product quality was obtained at a recirculating feed pH range of 8.5-8.9.

Detailed Description Text (58):

The data shows that the resistivity of second pass permeate could vary, and good quality water could still be obtained. The high purity water or third pass permeate had a total inorganic carbon (TIC) level of about 6 ppb, and the second pass permeate had a TIC of about 20 ppb. Thus, the third pass was effective in reducing TIC. It can also be seen that it is important to match the feed pH to the particular membrane selected. High purity water was obtained despite the fact that the single reverse osmosis module used in the third pass was operated at a recovery higher than recommended, indicating that further improvement is possible.

Detailed Description Text (61):

This example is the same as Example 1, except a non-charged polyamide membrane was used in the third pass reverse osmosis unit.

Detailed Description Text (64):

The 3 megohm-cm water obtained is only slightly better than can be obtained with two passes. Although this membrane has a nominal salt rejection slightly lower than the membrane used in Example 1 (99.0% minimum versus 99.5% minimum), the difference does not seem to account for the difference in performance.

Detailed Description Text (65):

This example illustrates that a conventional polyamide membrane, when used in the third pass does not achieve results comparable with the positively charged membrane of Example 1, where optimum pH is close to 9. The lower resistivity resulting from the use of a non-charged polyamide membrane is explained by the fact that at low operating pH (.ltoreq.8.3) carbon dioxide is present in second pass product. Carbon dioxide in second pass product passes to the third pass product, depressing pH and raising the conductivity. Bicarbonate passing through the third pass membrane enters into a lower pH environment on the permeate side splitting further to carbon dioxide depressing pH and raising conductivity.

Detailed Description Text (66):

At a pH of about 7.6 and above, salt rejection of the membrane falls, more fixed ions pass through the membrane, and conductivity is again increased.

Detailed Description Text (68):

This example is the same as Example 2 except that a dealkalizing and degassing system was used between the second and third passes. In the dealkalization/degassing step, the second permeate was maintained at a pH of about 4 and then passed over a membrane under vacuum on the opposite side. A nitrogen sweep was provided in the vacuum side to aid removal of gas. The degassed liquid was introduced to the third pass reverse osmosis module. The third pass permeate had a resistivity of 10.8 megohm-cm at a pH of 7. It will be seen that the dealkalization/degassing step resulted in higher purity product water when compared to Example 2.

Other Reference Publication (1):

Tai et al, "Removal of Dissolved Oxygen in Ultrapure Water Production Using Microporous Membrane Modules", J. Membrane Sci. 37 (1994)99-105.

CLAIMS:

1. A method for producing high purity product water using a three pass reverse osmosis system, the method having the ability to produce water having a resistivity in the range of 10 to 18 megohm-cm, the method comprising the steps of:

(a) providing a feedwater to be purified, said feedwater having a basic pH;

(b) introducing the feedwater to a high pressure side of a first reverse osmosis membrane module comprising a non-charged membrane;

(c) passing water through said first reverse osmosis membrane to provide a first retentate and a first permeate, said first permeate maintained at a basic pH;

(d) transferring said first permeate to a high pressure side of a second reverse osmosis membrane module comprising a non-charged membrane;

(e) further purifying said first permeate by passing at least a portion thereof through said second reverse osmosis membrane to provide a second retentate and a second permeate having a pH of less than 6.2 and resistivity in the range of 0.5 to 2.5 megohm-cm;

(f) adjusting said second permeate to a pH in the range of 6.2 to 8.5 to provide an adjusted second permeate;

(g) providing a third pass reverse osmosis module having a third high pressure side and a third low pressure side, said third pass reverse osmosis module comprising a third pass reverse osmosis membrane selected from a positively charged membrane and a negatively charged membrane;

(h) introducing said adjusted second permeate to the high pressure side of said third pass reverse osmosis module; and

(i) passing at least a portion of said adjusted second permeate through said third pass reverse osmosis membrane to permeate high purity product water having a pH in the range of 6.8 to 7.2.

2. A method for producing high purity product water using a three pass reverse osmosis system, the method having the ability to produce water having a resistivity in the range of 10 to 18 megohm-cm, the method comprising the steps of:

(a) providing a feedwater to be purified;

(b) introducing the feedwater to a high pressure side of a first reverse osmosis membrane module;

(c) passing water through said first reverse osmosis membrane to provide a first retentate and a first permeate;

(d) transferring said first permeate to a high pressure side of a second reverse osmosis membrane module;

(e) further purifying said first permeate by passing at least a portion thereof through said second reverse osmosis membrane to provide a second retentate and a second permeate having a pH of less than 6 and having an alkalinity of less than 0.2 mg/l and a resistivity in the range of 0.5 to 2.5 megohm-cm;

(f) adjusting said second permeate to a pH in the range of 7.5 to 8.5 to provide an adjusted second permeate;

(g) providing a third pass reverse osmosis membrane having a third high pressure side and a third low pressure side, said third pass reverse osmosis membrane having a positively charged membrane to reject monovalent positively charged ions;

(h) introducing said adjusted second permeate to the high pressure side of said third pass reverse osmosis membrane; and

(i) passing at least a portion of said adjusted second permeate through said third pass, positively charged, reverse osmosis membrane thereby rejecting positively charged monovalent ions to produce said high purity product water having a pH in the range of 6.8 to 7.2.

3. The method in accordance with claim 2 including using a non-charged reverse osmosis membrane in said first and second reverse osmosis modules.

6. A method for producing high purity product water using a three pass reverse osmosis system, the method having the ability to produce water having a resistivity in the range of 10 to 18 megohm-cm, the method comprising the steps of:

(a) providing a feedwater to be purified;

(b) introducing the feedwater to a high pressure side of a first reverse osmosis membrane module;

(c) passing water through said first reverse osmosis membrane to provide a first retentate and a first permeate;

(d) transferring said first permeate to a high pressure side of a second reverse osmosis membrane module;

(e) further purifying said first permeate by passing at least a portion thereof through said second reverse osmosis membrane to provide a second retentate and a second permeate having a pH of less than 6.2 and resistivity in the range of 0.5 to 2.5 megohm-cm;

(f) adjusting said second permeate to a pH in the range of 6 to 9.5 to provide an adjusted second permeate;

(g) providing a third pass reverse osmosis module having a third high pressure side and a third low pressure side, said third pass reverse osmosis module comprising a third pass reverse osmosis membrane selected from a positively charged membrane and a negatively charged membrane;

(h) introducing said adjusted second permeate to the high pressure side of said third pass reverse osmosis module;

(i) passing at least a portion of said adjusted second permeate through said third pass reverse osmosis membrane to permeate high purity product water having a pH in the range of 6.8 to 7.2;

(j) measuring the resistance of the high purity product water produced at said third low pressure side of said third reverse osmosis unit to provide a resistance measurement;

(k) relaying said resistance measurement to a programmable logic controller;

(l) in said programmable controller, comparing said resistance measurement with a previous resistance measurement to provide a comparison; and

(m) in response to said comparison, maintaining or changing the pH of at least one said feedwater first permeate and said second permeate upwardly or downwardly to produce said high purity water having said desired resistivity.

7. The method in accordance with claim 6 including adjusting said second permeate to a pH in the range of 7 to 8.5, an alkalinity of less than 0.2 mg/l (as CaCO.sub.3) and using in said third pass reverse osmosis module a positively charged membrane.

8. The method in accordance with claim 6 including providing a said second permeate with a pH in the range of 6.2 to 7.5 and CO.sub.2 level of less than 200 PPB and using in said third pass reverse osmosis module a negatively charged membrane for rejecting negatively charged monovalent ions.

9. The method in accordance with claim 6 including using a negatively charged membrane in said third pass reverse osmosis module for rejecting monovalent negatively charged ions and degassing said second permeate to remove molecular CO.sub.2 prior to adjusting the pH of said second permeate.

13. The method in accordance with claim 6 including the step of subjecting said feedwater to a filtration step selected from microfiltration and nanofiltration.

14. A method for producing high purity product water using a three pass reverse osmosis system, the method having the ability to produce water having a resistivity in the range of 10 to 18 megohm-cm, the method comprising the steps of:

- (a) providing a feedwater to be purified;
 - (b) introducing the feedwater to a high pressure side of a first reverse osmosis membrane module
 - (c) passing water through said first reverse osmosis membrane to provide a first retentate and a first permeate;
 - (d) transferring said first permeate to a high pressure side of a second reverse osmosis membrane module;
 - (e) further purifying said first permeate by passing at least a portion thereof through said second reverse osmosis membrane to provide a second retentate and a second permeate;
 - (f) adjusting said second permeate to a pH in the range of 7.5 to 8.5 to provide an adjusted second permeate;
 - (g) providing a third pass reverse osmosis membrane having a third high pressure side and a third low pressure side, said third pass reverse osmosis membrane having a positively charged membrane;
 - (h) introducing said adjusted second permeate to the high pressure side of said third pass reverse osmosis membrane;
 - (i) passing at least a portion of said adjusted second permeate through said third pass positively charged reverse osmosis membrane to produce a third permeate, high purity product water having a pH in the range of 6.8 to 7.2 and a resistivity in the range of 10 to 18 megohm-cm;
 - (j) measuring the resistance of the high purity product water produced in said third reverse osmosis unit to provide a resistance measurement;
 - (k) relaying said resistance measurement to a programmable logic controller;
 - (l) in said programmable controller, comparing said resistance measurement with a previous resistance measurement to provide a comparison; and
 - (m) in response to said comparison, maintaining or changing the pH of at least one of said second pass reverse osmosis permeate and said feedwater upwardly or downwardly to produce said high purity water having said desired resistivity.
15. The method in accordance with claim 14 including using a non-charged reverse osmosis membrane in at least one of said first and second reverse osmosis modules.
18. The method in accordance with claim 14 including using a positively charged membrane in at least one of said first and second reverse osmosis modules.
19. A three pass reverse osmosis system for making high purity water having a resistivity in the range of 10 to 18 megohm-cm, the system comprised of:
- (a) a first reverse osmosis module having a first high pressure side and a first low pressure side;
 - (b) means for introducing feedwater to the high pressure side of said first reverse osmosis membrane module;
 - (c) means for passing water through said first reverse osmosis membrane to provide a first retentate and a first permeate;

(d) a second reverse osmosis module having a second high pressure side and a second low pressure side, said second high pressure side adapted to receive said first permeate from said first low pressure side, said second reverse osmosis module adapted for further purifying said first permeate by passing at least a portion thereof through said second reverse osmosis membrane to provide a second retentate and a second permeate having a pH of less than about 6.2 and having an alkalinity of less than 0.2 mg/l (based on CaCO₃) and a resistivity in the range of 0.5 to 2.5 megohm-cm;

(e) means for adjusting said second permeate to a pH in the range of about 6 to 8.5 to provide an adjusted second permeate;

(f) a third pass reverse osmosis membrane module having a third high pressure side for receiving said adjusted second permeate and a third low pressure side, said third pass reverse osmosis membrane having a positively or negatively charged membrane; and

(g) means for purifying at least a portion of said adjusted second permeate by passing it through said third pass reverse osmosis membrane module to provide said high purity product water having a pH in the range of 6.8 to 7.2 at said third low pressure side.

20. A method for producing high purity product water using a three pass reverse osmosis system, the method having the ability to produce water having a resistivity in the range of 10 to 18 megohm-cm, the method comprising the steps of:

(a) providing a feedwater to be purified, the feedwater having a pH in the range of about 8.3 to 11;

(b) introducing the feedwater to a high pressure side of a first reverse osmosis membrane module;

(c) passing water through said first reverse osmosis membrane to provide a first permeate and a first retentate, the first permeate maintained at a pH in the range of about 7 to 10;

(d) transferring said first permeate to a high pressure side of a second reverse osmosis membrane module;

(e) further purifying said first permeate by passing at least a portion thereof through said second reverse osmosis membrane to provide a second retentate and a second permeate having a pH of less than about 6.2 and resistivity in the range of 0.5 to 2.5 megohm-cm;

(f) adjusting said second permeate to a pH in the range of 6.2 to 8.5 to provide an adjusted second permeate;

(g) providing a third pass reverse osmosis module having a third high pressure side and a third low pressure side;

(h) introducing said adjusted second permeate to the high pressure side of said third pass reverse osmosis module; and

(i) passing at least a portion of said adjusted second permeate through said third pass reverse osmosis membrane to permeate high purity product water having a pH in the range of 6.8 to 7.2.

24. The method in accordance with claim 20 including the step of subjecting said feedwater to a filtration step selected from microfiltration and nanofiltration.

26. A method for producing high purity product water using a three pass reverse osmosis system, the method having the ability to produce water having a resistivity in the range of 10 to 18 megohm-cm, the method comprising the steps of:

(a) providing a feedwater to be purified, the feedwater having a pH in the range of about 8.3 to 11;

(b) introducing the feedwater to a high pressure side of a first reverse osmosis membrane module;

(c) passing water through said first reverse osmosis membrane to provide a first permeate and a first retentate, the first permeate maintained at a pH in the range of 7 to 10;

(d) transferring said first permeate to a high pressure side of a second reverse osmosis membrane module;

(e) further purifying said first permeate by passing at least a portion thereof through said second reverse osmosis membrane to provide a second retentate and a second permeate having a pH of less than 6.2 and having an alkalinity of less than 0.2 mg/l (based on CaCO₃) and a resistivity in the range of 0.5 to 2.5 megohm-cm;

(f) adjusting said second permeate to a pH in the range of 7.5 to 8.5 to provide an adjusted second permeate;

(g) providing a third pass reverse osmosis membrane having a third high pressure side and a third low pressure side;

(h) introducing said adjusted second permeate to the high pressure side of said third pass reverse osmosis membrane; and

(i) passing at least a portion of said adjusted second permeate through said third pass reverse osmosis membrane to produce said high purity product water having a pH in the range of 6.8 to 7.2.

27. A method for producing high purity product water using a three pass reverse osmosis system, the method having the ability to produce water having a resistivity in the range of 10 to 18 megohm-cm, the method comprising the steps of:

(a) providing a feedwater to be purified, the feedwater having a pH in the range of about 8.3 to 11;

(b) introducing the feedwater to a high pressure side of a first reverse osmosis membrane module;

(c) passing water through said first reverse osmosis membrane to provide a first permeate and a first retentate, the first permeate maintained at a pH in the range of about 7 to 10;

(d) transferring said first permeate to a high pressure side of a second reverse osmosis membrane module;

(e) further purifying said first permeate by passing at least a portion thereof through said second reverse osmosis membrane to provide a second retentate and a second permeate having a pH of less than about 6.2 and resistivity in the range of 0.5 to 2.5 megohm-cm;

(f) adjusting said second permeate to a pH in the range of 6.2 to 8.5 to provide an

adjusted second permeate;

(g) providing a third pass reverse osmosis module having a third high pressure side and a third low pressure side;

(h) introducing said adjusted second permeate to the high pressure side of said third pass reverse osmosis module;

(i) passing at least a portion of said adjusted second permeate through said third pass reverse osmosis membrane to permeate high purity product water having a pH in the range of 6.8 to 7.2;

(j) measuring the resistance of the high purity product water produced at said third low pressure side of said third reverse osmosis unit to provide a resistance measurement;

(k) relaying said resistance measurement to a programmable logic controller;

(l) in said programmable controller, comparing said resistance measurement with a previous resistance measurement to provide a comparison; and

(m) in response to said comparison, maintaining or changing the pH of at least one of said feedwater, said first permeate and said second permeate upwardly or downwardly to produce said high purity water having said desired resistivity.

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☐ 1. Document ID: US 6723241 B2

L1: Entry 1 of 5

File: USPT

Apr 20, 2004

US-PAT-NO: 6723241

DOCUMENT-IDENTIFIER: US 6723241 B2

TITLE: Composite membrane and method for making the same

DATE-ISSUED: April 20, 2004

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Mickols; William E.	Chanhassen	MN		

US-CL-CURRENT: 210/500.38; 210/490, 210/500.27

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw D
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☐ 2. Document ID: US 6562266 B2

L1: Entry 2 of 5

File: USPT

May 13, 2003

US-PAT-NO: 6562266

DOCUMENT-IDENTIFIER: US 6562266 B2

TITLE: Composite membrane and method for making the same

DATE-ISSUED: May 13, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Mickols; William E.	Chanhassen	MN		

US-CL-CURRENT: 264/41; 210/500.38, 264/48, 427/244, 427/245

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw D
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☐ 3. Document ID: US 6337018 B1

L1: Entry 3 of 5

File: USPT

Jan 8, 2002

US-PAT-NO: 6337018
DOCUMENT-IDENTIFIER: US 6337018 B1

TITLE: Composite membrane and method for making the same

DATE-ISSUED: January 8, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Mickols; William E.	Chanhassen	MN		

US-CL-CURRENT: 210/500.38; 210/490, 210/500.27, 264/48, 264/49, 427/244

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KNOW	Draw De
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☐ 4. Document ID: US 6280853 B1

L1: Entry 4 of 5

File: USPT

Aug 28, 2001

US-PAT-NO: 6280853
DOCUMENT-IDENTIFIER: US 6280853 B1

TITLE: Composite membrane with polyalkylene oxide modified polyamide surface

DATE-ISSUED: August 28, 2001

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Mickols; William E.	Chanhassen	MN		

US-CL-CURRENT: 428/474.4; 210/490, 210/500.23, 210/500.33, 210/500.35, 210/651,
210/652, 210/653, 210/654, 428/474.9, 428/475.5, 428/475.8, 428/476.1

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KNOW	Draw De
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☐ 5. Document ID: US 5755964 A

L1: Entry 5 of 5

File: USPT

May 26, 1998

US-PAT-NO: 5755964
DOCUMENT-IDENTIFIER: US 5755964 A

TITLE: Method of treating polyamide membranes to increase flux

DATE-ISSUED: May 26, 1998

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Mickols; William E.	Midland	MI		

US-CL-CURRENT: 210/500.37; 210/490, 210/500.38, 264/48

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Drawn De
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Terms	Documents
5755964	5

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L3: Entry 2 of 3

File: USPT

May 13, 2003

DOCUMENT-IDENTIFIER: US 6562266 B2

TITLE: Composite membrane and method for making the same

Brief Summary Text (9):

Methods of improving membrane performance by post-treatment are also known. For example, U.S. Pat. No. 5,876,602 to Jons et al. describes treating a polyamide composite membrane with an aqueous chlorinating agent to improve flux, lower salt passage, and/or increase membrane stability to base. U.S. Pat. No. 5,755,964 to Mickols discloses a process wherein the polyamide discriminating layer is treated with ammonia or selected amines, e.g., butylamine, cyclohexylamine, and 1,6 hexane diamine. U.S. Pat. No. 4,765,897 to Cadotte discloses the post treatment of a membrane with a strong mineral acid followed by treatment with a rejection enhancing agent. U.S. Pat. Nos. 4,765,897; 5,876,602 and 5,755,964 are incorporated herein by reference.

Brief Summary Text (35):

One means for determining whether the subject complexing agent(s) have been successfully contacted with the acyl halide in accordance to the subject method is the presence of a "detectable quantity" of "retained" complexing agent in the polyamide membrane. The term "retained" is intended to mean complexing agent which remains (e.g., associated, covalently bonded, complexed, weakly bound, etc.) within the polyamide membrane even after the membrane has been subjected to operation in reverse osmosis mode using pure water feed at a 24 gfd (gallons per square foot per day) (0.0011 cm/sec) flux rate through the membrane with a permeate recovery between 0.5% to 25% at 25.degree. C. for 24 hours. This may be accomplished by use of test cells commonly used to test membranes. For example, the test cell may be of a "plate and frame" design or may include preparing a spiral wound element with the membrane.

Brief Summary Text (73):

The membranes of the present invention may be subjected to various post treatments as described in U.S. Pat. Nos. 4,765,897; 5,876,602 and 5,755,964, all of which are incorporated herein by reference. Such post treatments may further enhance membrane performance, e.g., increased flux and/or decreased salt passage.

Brief Summary Text (75):

Another example of an applicable post treatment is described in U.S. Pat. No. 5,755,964, which comprises contacting the discriminating layer with an amine from the group consisting of: ammonia optionally substituted with one or more alkyl groups of one to two carbons which alkyl groups may be further optionally substituted with one or more substituents selected from hydroxy, phenyl, or amino; butylamine; cyclohexylamine; 1,6-hexanediamine and mixtures thereof. Preferred substituted ammonia substances include those such as dimethylamine; trimethylamine; ethylamine; triethanolamine; N,N-dimethyl ethanolamine; ethylenediamine; and benzylamine. It has been discovered that by contacting the above amines with the discriminating layer, the flux is increased and the rejection rates for particular substances may be changed. The degree that the flux of the membrane is increased or enhanced may be controlled by varying the particular amine employed, the concentration of the amine, the time of contact between the discriminating layer and amine, the temperature of the contact, the pH of the amine solution, or

combinations thereof. As the flux is increased, the selectivity of the membrane may change, i.e., the membrane may allow univalent ions such as sodium to pass through the membrane at a higher rate while only rejecting divalent ions and organic compounds.

US Reference Patent Number (17):

5755964

US Reference Group (17):

5755964 19980500 Mickols 210/500.37

Other Reference Publication (4):

Derwent Abstract, JP2000015067A, Manufacture of Composite Semipermeable Membrane for Recovery of Electrode Deposition Paints and Pure Water for Washing Semiconductor, etc. with available selected translated excerpts from patent.

CLAIMS:

2. The method of claim 1 wherein the step of contacting the complexing agent with the polyfunctional acyl halide results in a polyamide layer having a detectable quantity of the binding core of the complexing agent retained therein after the membrane has been operated in reverse osmosis mode using pure water feed at a 24 gfd flux rate through the membrane with a permeate recovery between 0.5% to 25% at 25.degree. C. for 24 hours.

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☐ 1. Document ID: US 20030015470 A1

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L1: Entry 1 of 1

File: PGPB

Jan 23, 2003

PGPUB-DOCUMENT-NUMBER: 20030015470

PGPUB-FILING-TYPE: new

DOCUMENT-IDENTIFIER: US 20030015470 A1

TITLE: Nanofiltration water-softening apparatus and method

PUBLICATION-DATE: January 23, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Muralidhara, Harapanahalli S.	Plymouth	MN	US	
Lee, Robert Sung	Minnetonka	MN	US	
Aschauer, Martin N.	Port Huron	MI	US	

US-CL-CURRENT: 210/650; 210/321.6, 210/651

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	Claims	KOMC	Drawn De
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Terms	Documents
nanofiltration same sr1	1

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L2: Entry 2 of 4

File: USPT

Dec 3, 2002

US-PAT-NO: 6488847

DOCUMENT-IDENTIFIER: US 6488847 B2

**** See image for Certificate of Correction ****

TITLE: Process and equipment for recovering developer from photoresist development waste and reusing it

DATE-ISSUED: December 3, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Sugawara; Hiroshi	Omiya			JP

ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE CODE
Organo Corporation	Tokyo			JP	03

APPL-NO: 09/ 757368 [PALM]

DATE FILED: January 9, 2001

PARENT-CASE:

This application is a division of U.S. Ser. No. 09/392,433, filed on Sep. 9, 1999, and now U.S. Pat. No. 6,187,519.

FOREIGN-APPL-PRIORITY-DATA:

COUNTRY	APPL-NO	APPL-DATE
JP	10-309606	October 30, 1998

INT-CL: [07] C02 F 9/02, C02 F 9/08, G03 C 5/00

US-CL-ISSUED: 210/259; 210/96.1, 210/143, 210/259, 210/263, 210/685, 210/167, 210/195.1, 430/398, 430/399

US-CL-CURRENT: 210/259; 210/143, 210/167, 210/195.1, 210/263, 210/685, 210/96.1, 430/398, 430/399

FIELD-OF-SEARCH: 210/96.1, 210/101, 210/143, 210/167, 210/670, 210/681, 210/685, 210/686, 210/688, 137/88, 137/571, 137/572, 118/603, 430/398, 430/399, 366/132, 366/151.1, 366/152.1, 222/1, 222/59, 222/151, 222/152

PRIOR-ART-DISCLOSED:

U.S. PATENT DOCUMENTS

Search Selected

Search ALL

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	PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<input type="checkbox"/>	<u>4606827</u>	August 1986	Ernstson et al.	210/670
<input type="checkbox"/>	<u>5148945</u>	September 1992	Geatz	222/1
<input type="checkbox"/>	<u>5330072</u>	July 1994	Ferri et al.	222/1
<input type="checkbox"/>	<u>5354434</u>	October 1994	Satoh et al.	204/72
<input type="checkbox"/>	<u>5405508</u>	April 1995	Kawakami et al.	204/102
<input type="checkbox"/>	<u>5670340</u>	September 1997	Juers	430/399
<input type="checkbox"/>	<u>5821036</u>	October 1998	Fiener et al.	430/326
<input type="checkbox"/>	<u>5874049</u>	February 1999	Ferri et al.	366/132
<input type="checkbox"/>	<u>5874204</u>	February 1999	Sugawara et al.	430/399
<input type="checkbox"/>	<u>6083670</u>	July 2000	Sugawara et al.	430/399

FOREIGN PATENT DOCUMENTS

FOREIGN-PAT-NO	PUBN-DATE	COUNTRY	US-CL
2332957	July 1999	GB	
58030753	February 1983	JP	
407328642	December 1995	JP	
10085741	April 1998	JP	

OTHER PUBLICATIONS

Kokai Hei 5-40345, Feb. 19, 1993, Japan-Abstract.
Derwent of JP Kokai Hei 5-40345, 1993.
PAJ of JP Kokai Hei 5-40345, 1993.

ART-UNIT: 1723

PRIMARY-EXAMINER: Drodge; Joseph W.

ATTY-AGENT-FIRM: Norris McLaughlin & Marcus

ABSTRACT:

A tetraalkylammonium hydroxide (TAAH) solution recovered from a development waste through separation therefrom of impurities such as photoresist is mixed with a surface-active substance to have the surface tension thereof adjusted to a desired one, and then reused as a rejuvenated developer. Thus, the surface-active effect (wetting properties) of the rejuvenated developer recovered from the development waste is properly adjusted and controlled, whereby fine photoresist patterns can be stably and effectively developed. Usable surface-active substances include surfactants, and dissolved photoresist contained in the development waste or a photoresist-containing solution such as a photoresist-containing treated solution derived therefrom. Examples of the method of mixing the recovered TAAH-containing solution with the photoresist-containing solution to prepare the rejuvenated developer include a method wherein the TAAH concentration thereof is adjusted either after or while mixing the two solutions, and a method wherein the TAAH concentrations of the two solutions are respectively adjusted, followed by mixing

the two solutions at a proper proportion.

16 Claims, 10 Drawing figures
Exemplary Claim Number: 1
Number of Drawing Sheets: 10

BRIEF SUMMARY:

1 BACKGROUND OF THE INVENTION

2 1. Field of the Invention

3 The present invention relates to process and equipment for covering a developer from a photoresist development waste and reusing it, and particularly to process and equipment for recovering a developer from a photoresist development waste, discharged from a process of producing electronic parts such as semiconductor devices (LSI, VLSI, etc.), liquid crystal displays (LCD) or printed boards, or the like, and reusing it.

4 2. Related Art

5 In the field of manufacturing electronic parts such as semiconductor devices and liquid crystal displays, and the like, integration scale-up and miniaturization of products have been in rapid progress. For example, the procedure of manufacturing such electronic parts includes a photolithographic process, wherein a photoresist film is formed on a substrate such as a wafer or a glass substrate, predetermined parts of the film are then irradiated with a light or the like, and subsequently the photoresist film is developed with a developer to form a fine pattern. Herein, photoresists include positive photoresists that turn soluble in a developer where exposed to a light or the like, and negative photoresists that turn insoluble in a developer where exposed to a light or the like. In the field of manufacturing electronic parts such as semiconductor devices and liquid crystal displays, positive photoresists are predominantly used. An aqueous solution of a tetraalkylammonium hydroxide (hereinafter often referred to in brief as "TAAH") such as tetramethylammonium hydroxide (hereinafter often referred to in brief as "TMAH") or trimethyl(2-hydroxyethyl)ammonium hydroxide (i.e., choline) as an organic alkali is usually used as a developer for such positive photoresists. Incidentally, although the mainstream developers for the negative photoresists are organic solvent developers, alkali developers may also be used for some negative photoresists.

6 A photoresist as material to be developed is a hydrophobic substance, and an aqueous solution of TAAH such as TMAH is hydrophilic, whereby the interfacial affinity therebetween is poor. Because of the poor interfacial affinity of the aqueous TAAH solution for the photoresist, effective development of fine patterns is difficult with the aqueous TAAH solution as an ordinary alkali developer. In order to solve this problem, alkali developers containing a surfactant have already been marketed and put into practical use (e.g., developer commercially available under the trade name of "NMD-W" and manufactured by Tokyo Ohka Kogyo Co., Ltd.).

7 Meanwhile, waste discharged from the development step of using an aqueous TAAH solution as the alkali developer in the photolithographic process (called "photoresist development waste" and hereinafter often referred to in brief as "development waste") usually contains the dissolved photoresist and TAAH, and is hard to render harmless through any treatments. Thus, it is desired to

recover and reuse TAAH because of its adverse effects on environment, and various attempts have been made to develop a method of recovering and rejuvenating an alkali developer (hereinafter often referred to as "developer"). Examples of such a method include methods comprising electrodialysis or electrolysis (Japanese Patent Laid-Open No. 7-328642 published on Dec. 19, 1995, and Japanese Patent Laid-Open No. 5-17889 published on Jan. 26, 1993), a method using an anion exchange resin (Japanese Patent Laid-Open No. 10-85741 published on Apr. 7, 1998), a method comprising electrodialysis or electrolysis and using an ion exchange resin(s) (U.S. Pat. No. 5,874,204 patented on Feb. 23, 1999), a method comprising neutralization and electrolysis (Japanese Patent Laid-Open No. 7-41979 published on Feb. 10, 1995), a method using activated carbon (Japanese Patent Laid-Open No. 58-30753 published on Feb. 23, 1983), and a method using a nanofiltration membrane (NF membrane) [Japanese Patent Laid-Open No. 11-192481 published on Jul. 21, 1999].

8 Since TAAH-containing developers recovered by these methods contain no substantial surface-active substances, however, they are highly hydrophilic solutions. Even where a surfactant is contained in a virgin developer, the recovered TAAH-containing developer has a decreased surfactant concentration, which makes it difficult to secure a surface-active effect comparable to that of the virgin developer, thereby posing a problem that it cannot be reused as a developer in the same development step as it is.

9 Accordingly, an object of the present invention is to provide process and equipment for recovering a developer from a photoresist development waste and reusing it, which can give a rejuvenated developer capable of stably and effectively developing fine patterns of a photoresist by proper adjustment and control of the surface-active effect (wetting properties) of a TAAH-containing solution recovered from the development waste.

10 SUMMARY OF THE INVENTION

11 The present invention provides a process for recovering a developer from a photoresist development waste and reusing it; comprising separating impurities including photoresist from a photoresist development waste for recovering a tetraalkylammonium hydroxide solution, and mixing the recovered tetraalkylammonium hydroxide solution with a surface-active substance.

12 Since the TAAH-containing developer is hydrophilic as against the hydrophobic photoresist, the interfacial affinity therebetween is so weak that photoresist films become harder to effectively develop not only in the horizontal direction but also in the depthwise direction as the patterns of development become finer. In view of this, there are developers admixed with a surface-active substance such as a surfactant with the aim of weakening the surface tensions of the developers as described before. Meanwhile, the development waste discharged from the development step of using a TAAH-containing developer contains the dissolved photoresist component. This photoresist component has a surface-active effect because it is a water-soluble polymeric substance.

13 In the conventional methods of recovering and reusing a TAAH-containing developer, however, part or the whole of any surface-active substances including the photoresist component is removed. This will be described below in connection with individual unit operations usable in these methods. (1) Since surface-active substances such as a photoresist and a surfactant, even if endowed with an electric charge, are hardly concentrated in either electrodialysis or electrolysis because these comparatively high molecular

weight substances do not migrate through a diaphragm such as an ion exchange membrane. This is particularly true of nonionic surface-active substances, which migrate such a diaphragm only slightly by diffusion. (2) A surface-active substance having an electric charge is removed by an ion exchange resin. (3) Surface-active substances are generally adsorbed on activated carbon. (4) Surface-active substances are removed into concentrate with a nanofilter because they are high in molecular weight.

- 14 In view of the foregoing, according to the present invention, the recovered developer stripped of any surface-active substances including the photoresist component is mixed with a suitable amount of a surface-active substance such as a surfactant or the photoresist to adjust the surface tension thereof to a predetermined one, and then reused as a developer.
- 15 The usable surface-active substance to be mixed, though varied depending on the development step and the like, may usually be one or a plurality of surface-active substances selected from commercially available surface-active substances such as nonionic, anionic and cationic surfactants. Where a surface-active substance is contained in a virgin developer, the same surface-active substance as contained in that developer is desirably used.
- 16 Since the dissolved photoresist component contained in the photoresist development waste also has a surface-active effect, a photoresist-containing solution such as the photoresist development waste or a photoresist-containing treated solution derived therefrom may alternatively be added to the recovered developer (TAAH solution) depleted of any surface-active substance(s) such as the photoresist component to adjust the surface tension thereof to a predetermined level, followed by reusing the resultant rejuvenated developer.
- 17 In this case, the photoresist (surface-active substance) concentration can favorably be adjusted and controlled using an ultraviolet-visible light absorptiometer by taking advantage of the fact that the photoresist has absorptions in the ultraviolet and visible light regions (Japanese Patent Laid-Open No. 10-207082 published on Aug. 7, 1998). Of course, however, any apparatuses capable of measuring the photoresist concentration can be used without limitation to ultraviolet-visible light absorptiometers.
- 18 Where a TAAH-containing solution recovered by a conventional method or the like is to be mixed with a photoresist-containing solution such as the photoresist development waste or a photoresist-containing treated solution derived therefrom, examples of the method of adjusting the rejuvenated developer, though not particularly limited, include a method wherein the TAAH concentration is adjusted either after or while mixing the recovered TAAH-containing solution with the photoresist-containing solution, and a method wherein the recovered TAAH-containing solution and the photoresist-containing solution are respectively adjusted in TAAH concentration and then mixed at a proper proportion. (Ultra)pure water and/or "TAAH or an aqueous solution thereof" [hereinafter referred to as "TAAH (aqueous solution)"] may be used for adjustment of the TAAH concentration(s).
- 19 Where much metallic impurities such as Na, Fe and Al are contained in the photoresist-containing solution, such as the photoresist development waste or the photoresist-containing treated solution derived therefrom, to be mixed with the recovered TAAH-containing solution to impart a surfaceactive effect to the latter, such metallic impurities are preferably removed with a cation exchange resin in the hydrogen ion form (H form) or in the tetraalkylammonium ion form (TAA form) and/or a chelate resin before the photoresist-containing solution is mixed with the recovered TAAH-containing solution.

- 20 The photoresist development waste will now be described. The development waste usually contains the dissolved photoresist and TAAH. In general, however, waste (wastewater), which differs from factory to factory, may be mixed with any foreign matter, and may sometimes be mixed with other wastewater as the case may be, whereby part of the hydroxide ions of TAAH may possibly be replaced with other anions to form a salt(s) of tetraalkylammonium (hereinafter often referred to in brief as "TAA"). The foregoing development waste is usually alkaline with a pH value of 12 to 14. The photoresist is dissolved in the form of a salt with TAA ions in the alkaline development waste due to its acid groups such as carboxyl groups and phenolic hydroxyl groups.
- 21 Examples of such other anions, which differ from factory to factory, include inorganic anions such as fluoride ions, chloride ions, bromide ions, carbonate ions, hydrogencarbonate ions, sulfate ions, hydrogensulfate ions, nitrate ions, phosphate ions, hydrogenphosphate ions and dihydrogenphosphate ions, and organic anions such as formate ions, acetate ions, and oxalate ions. Carbonate ions and hydrogencarbonate ions may often exist in small amounts because carbon dioxide gas in the air is liable to dissolve in the development waste. Additionally stated, since the counter ions of TAA ions in concentrate obtained through electrolysis as described later are usually hydroxide ions, incorporation of at least an electrolysis step into the method of recovering a TAAH solution will suffice when the amount of anions other than hydroxide ions is so large that a difficulty is encountered in reusing the resultant TAAH solution as a photoresist alkali developer.
- 22 Examples of TAAH in the development waste, which is an alkali used in the photoresist developer for use in production of various electronic parts and the like, include tetramethylammonium hydroxide (TMAH), tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, methyltriethylammonium hydroxide, trimethylethylammonium hydroxide, dimethyldiethylammonium hydroxide, trimethyl(2-hydroxyethyl)ammonium hydroxide (i.e., choline), triethyl(2-hydroxyethyl)ammonium hydroxide, dimethyldi(2-hydroxyethyl)ammonium hydroxide, diethyldi(2-hydroxyethyl)ammonium hydroxide, methyltri(2-hydroxyethyl)ammonium hydroxide, ethyltri(2-hydroxyethyl)ammonium hydroxide, and tetra(2-hydroxyethyl)ammonium hydroxide (the former two and choline in particular).
- 23 Various methods can be mentioned as the method of separating impurities such as photoresist from a development waste to recover a TAAH solution. Preferred is a method comprising subjecting the development waste to at least one step selected from among a concentration and refining step (A) of concentrating and refining TAAH by at least one of electrodialysis and electrolysis (Japanese Patent Laid-Open No. 7-328642 and Japanese Patent Laid-Open No. 5-17889, incorporated herein by reference in their entirety), an ion exchange treatment step (B) of contact treatment with an anion exchanger (preferably an anion exchange resin desirably in the OH form in an aspect of refining) or with the above-mentioned anion exchanger and a cation exchange resin in one of the H form and the TAA form (Japanese Patent Laid-Open No. 10-85741 and U.S. Pat. No. 5,874,204, incorporated herein by reference in their entirety), and an NF membrane separation treatment step (C) of obtaining permeate mainly containing TAAH by treatment with a nanofiltration membrane (NF membrane) [Japanese Patent Laid-Open No. 11-192481, incorporated herein by reference in its entirety once laid open although it has not yet been published]. When a plurality of such steps are taken, the order thereof may be arbitrary, and any proper order thereof may be chosen, for example, in accordance with the purpose. The steps (A), (B) and (C) can all remove impurities as steps of refining the development waste or a TAAH-containing treated solution derived

therefrom. Among them, the step (B) in particular is a desirable step for removing impurities as much as possible, and the step (A) can concentrate TAAH.

- 24 A concentration step of concentrating TAAH by at least one of reverse osmosis treatment and evaporation may be taken though it is not a step capable of refining the development waste or the TAAH-containing treated solution derived therefrom unlike the concentration and refining step (A). Since the development waste is usually lowered in TAAH concentration with washing water (rinse water) and the like, a concentration step of concentrating TAAH from the development waste or the TAAH-containing treated solution derived therefrom by at least one of reverse osmosis treatment, evaporation, electrodialysis, electrolysis, etc. is preferably incorporated into the method of recovering a TAAH solution. Reverse osmosis treatment and evaporation concentrate TAAH concurrently with impurities such as photoresist, whereas electrodialysis and electrolysis are characterized by heightening the TAAH purity since impurities such as photoresist are not substantially concentrated simultaneously.
- 25 Where a plurality of such concentration methods are used in combination, the order thereof is not particularly limited but may be arbitrary. For example, however, when reverse osmosis membrane treatment and/or evaporation is followed by electrodialysis and/or electrolysis, there can be obtained advantages such as an improvement in current efficiency during electrodialysis and/or electrolysis, miniaturization and running cost reduction of an electrodialysis and/or electrolysis unit(s) due to a decrease in the amount of the solution to be treated therewith, lowering of a voltage to be applied to such a unit(s), and an improvement in TAAH recovery (U.S. Pat. No. 5,874,204). When the ion exchange treatment step (B) and/or the NF membrane separation treatment step (C) is also taken in this case, this evaporation and/or reverse osmosis membrane treatment step may be taken at any stage, e.g., at first, later or between both. Incidentally, since either condensed water obtained by evaporation or permeate water obtained by reverse osmosis membrane treatment does not substantially contain the photoresist and TAAH, the water can be used as process water or the like. In the case of reverse osmosis membrane treatment, the solution to be treated thereby preferably has a pH value of 9 to 12 from the standpoint of minimizing the deterioration of a reverse osmosis membrane.
- 26 From the standpoint of obtaining a high-purity rejuvenated developer, the anion exchanger for use in the step (B) is preferably an anion exchange resin, especially desirably an anion exchange resin in the OH form, which is desirably used in combination with a cation exchange resin in at least one of the H form and the TAA form, which can remove impurities such as Na. Other anion exchanger may sometimes be used instead of the anion exchange resin.
- 27 Incidentally, when the development waste or the TAAH-containing treated solution derived therefrom [e.g., TAAH solution obtained from the step (A) and/or (C)] is brought into contact with the anion exchange resin, the photoresist in the waste or the treated solution thereof can be highly selectively adsorbed on the anion exchange resin despite the coexistence of competitive hydroxide ions derived from TAAH. The reason for this is believed to be as follows: The mainstream alkali-developable photoresists are those having a novolak resin as the matrix resin. This novolak resin has a large number of benzene rings. When a styrene type anion exchange resin having benzene rings or the like resin in particular is, for example, used as the anion exchange resin, it is believed that the photoresist can be efficiently and highly selectively removed due to affinity (hydrophobic) interaction between the respective benzene rings of the anion exchange resin and the

photoresist in addition to the mutual electrostatic interaction thereof.

- 28 The NF membrane separation treatment step (C) may be taken in multiple stages (Japanese Patent Laid-Open No. 11-192481). In the step (C), concentrate mainly containing impurities such as photoresist is obtained together with permeate mainly containing TAAH. The NF membrane to be used in the step (C) is a separation membrane having a molecular cutoff falling within the range of 100 to 1,000 and characterized by a sodium chloride rejection of at most 90% when a 0.2% (wt./vol.) aqueous solution of sodium chloride as a solution to be treated is subjected to separation treatment with the membrane at 25.degree. C.
- 29 When the development waste or a TAAH-containing solution derived therefrom is treated with the NF membrane, most of TAAH permeates through the NF membrane to enter the permeate, while little or a little photoresist permeates through the NF membrane to remain mostly in the concentrate, wherein the photoresist is therefore concentrated. Further, some impurities such as metal components including Fe and Al, and silica, which are hard to remove in the ion exchange treatment step (B), can be removed into the concentrate because they little permeate through the NF membrane.
- 30 Since the permeate stripped of most of impurities is obtained in the NF membrane separation treatment step (C), the load of impurities can be decreased in any later step(s) such for example as the ion exchange treatment, electrodialysis and/or electrolysis step, if taken, to reduce the refining cost. Incidentally, the NF membrane separation treatment step (C) is inexpensive and easy of operation.
- 31 Examples of other step that may be incorporated into the method of separating impurities such as photoresist from a development waste to recover a TAAH solution include an activated carbon treatment step of bringing a development waste or a TAAH-containing treated solution derived therefrom into contact with activated carbon to remove the photoresist (Japanese Patent Laid-Open No. 58-30753, incorporated herein by reference in its entirety), and a chelate resin treatment step of bringing a development waste or a TAAH-containing treated solution derived therefrom into contact with a chelate resin to remove some metal impurities such as Fe and Al [Japanese Patent Application No. 10-265581 (i.e., 265,581/1998), incorporated herein by reference in its entirety once laid open although it has not yet been published]. Such other step(s) may be combined with at least one of the aforementioned steps, in which case the order thereof may be arbitrary.
- 32 Other methods of separating impurities such as photoresist from a development waste to recover a TAAH solution include methods wherein a development waste is subjected to a neutralization+solid-liquid separation step, a step of decomposing organics with ozone, hydrogen peroxide or ultraviolet ray irradiation, and an electrolysis concentration step in this order (Japanese Patent Laid-Open No. 4-41979 published on Jul. 12, 1992, Japanese Patent Laid-Open No. 5-17889 published on Jan. 26, 1993, and Japanese Patent Laid-Open No. 5-106074 published on Apr. 27, 1993, incorporated herein by reference in their entirety), and a method wherein a development waste is subjected to a neutralization+solid-liquid separation step and an electrolysis concentration step in this order. In such cases, most of the photoresist is removed by neutralization+solid-liquid separation, and a TAA salt formed by neutralization turns back to TAAH with the aid of electrolysis. When the purity of the TAAH-containing solution obtained by any method as mentioned above is insufficient, at least one of the aforementioned steps (A), (B) and (C), the chelate resin treatment step, and so on may be taken as a later step (s). When the TAAH-containing solution is low in TAAH concentration, an

evaporation and/or reverse osmosis membrane treatment step may be taken as a later step(s).

- 33 The principle of electrodialysis that may be effected as the step (A) will now be described while referring to FIG. 9. Incidentally, the description will be made of an ordinary case where TAA ions have hydroxide ions (OH.sup.-, hereinafter referred to as "OH ions") as the counter ions.
- 34 As shown in FIG. 9, cation exchange membranes 103 and anion exchange membranes 104 are arrayed alternately with each other between a cathode 101 and an anode 102 to form a plurality of cells. TAAH in a starting solution (development waste or TAAH-containing solution derived therefrom) containing TAAH and photoresist (R), and sent to the cells dissociates into TAA ions (TAA.sup.+) as cations and OH ions as anions. When a DC electric current is applied between the cathode 101 and the anode 102, therefore, TAA ions are transferred toward the cathode across a cation exchange membrane 103 but substantially blocked by an anion exchange membrane 104 next thereto, while OH ions are transferred toward the anode across an anion exchange membrane 104 but substantially blocked by a cation exchange membrane 103 next thereto. Thus, TAAH is concentrated in a given cell, while TAAH is depleted in cells adjacent to that cell. More specifically, a cell (A) having an anion exchange membrane 104 facing the cathode 101 functions as a concentrating cell wherein TAAH is concentrated to form concentrate, while a cell (B) having an anion exchange membrane 104 facing the anode 102 functions as a desalting cell wherein TAAH is depleted to form a desalted solution. Since the photoresist (R) in the starting solution hardly moves across the ion exchange membranes, the photoresist (R) is passed substantially as such through every concentrating cell and every desalting cell to remain in the concentrate and the desalted solution.
- 35 As is apparent from the foregoing, when the starting solution is passed through both the desalting cells and the concentrating cells as shown in FIG. 9, the photoresist (R) remains intact in the concentrate, and only TAAH is concentrated in the concentrating cells without concentration therein of the photoresist (R), whereby the photoresist concentration of the concentrate is almost the same as that of the starting solution. In this respect, electrodialysis is definitely different from evaporation and reverse osmosis wherein not only TAAH but also impurities such as photoresist are concentrated.
- 36 Where a high-purity TAAH solution reutilizable as a photoresist alkali developer is to be regenerated and recovered, a concentrate not substantially containing various impurities is preferably obtained through electrodialysis. For that purpose, it is preferred that (ultra)pure water or a solution of an electrolyte such as a low-concentration TAAH solution free of various impurities (e.g., a solution prepared by dissolving a small amount of virgin TAAH in pure or ultrapure water) be passed through the concentrating cells while passing the starting solution through the desalting cells. Where the starting solution is passed through the concentrating cells as well, however, an advantage is gained in respect of a decrease in the amount (volume) of wastewater discharged as desalted waste. In order to obtain a high-purity TAAH solution with a decrease in the amount of wastewater discharged as desalted waste, there also is preferably used such a method that permeate obtained by treating the starting solution containing TAAH and photoresist with an NF membrane be sent to concentrating cells while sending the starting solution or concentrate obtained through treatment thereof with the NF membrane to desalting cells. In any case, the desalted solution obtained by electrodialysis may be used as a source of photoresist as a surface-active substance either as such or after proper refining treatment thereof such as

ion exchange resin treatment and/or chelate resin treatment if necessary.

- 37 The electrodialysis unit may be one as is generally used. Examples of ion exchange membranes to be used in this unit, though not particularly limited in so far as capable of selectively separating either cations or anions, include ACIPLEX (registered trademark of products manufactured by Asahi Chemical Industry Co., Ltd.), SELEMION (registered trademark of products manufactured by Asahi Glass Co., Ltd.), NEOSEPTA (registered trademark of products manufactured by Tokuyama Soda Co., Ltd.), IonClad (registered trademark) electrically driven separation membranes (manufactured by Pall Company), and Nafion (registered trademark of products manufactured by E. I. du Pont de Nemours and Company). Properties of ion exchange membranes may be typical.
- 38 The structure of the electrodialysis unit is not particularly limited. For example, a plurality of cation exchange membranes and a plurality of anion exchange membranes may be stacked alternately with each other while maintaining appropriate intervals therebetween with gaskets provided either with an inflow port and an outflow port for a desalting solution, or with an inflow port and an outflow port for a concentrating liquid to form a plurality of cells, which are interposed between a pair of electrodes to construct an electrodialyzer.
- 39 The electrodialysis unit is not limited to the above-mentioned typical structure, but may alternatively be constructed in such a way that bipolar membranes are each disposed as diaphragms between the cation exchange membranes and the anion exchange membranes, for example, as disclosed in Japanese Patent Laid-Open No. 6-299,385 published on Oct. 25, 1994 (incorporated herein by reference in its entirety).
- 40 As for the electrodes used herein, examples of the anode include those made of nickel, carbon, stainless steel or the like, and titanium electrodes coated with platinum or iridium, while examples of the cathode include those made of stainless steel, nickel or the like, and titanium electrodes coated with platinum or iridium. The anode and the cathode may be in any form, examples of which include a plate, a rod, a net, a porous plate.
- 41 Herein, neutral membranes such as polyvinyl alcohol membranes or hydrophilized porous Teflon (registered trademark of products manufactured by E. I. du Pont de Nemours and Company) membranes, which have a superior alkali resistance to that of anion exchange membranes, may be used instead of the anion exchange membranes. The neutral membranes, which are simple polymer membranes free of ionic functional groups, allow TAA ions to pass thereacross, but are lower in permeability thereto than cation exchange membranes. In this case, therefore, a difference in transference number between the neutral membranes and the cation exchange membranes is taken advantage of, whereby TAA ions can be concentrated by electrodialysis. When the neutral membranes are used instead of the anion exchange membranes, however, the current efficiency is worse than that in the case of the anion exchange membranes.
- 42 Examples of the foregoing electrodialysis, which may be done batch-wise, semi-batch-wise or continuously, include not only a single-stage method, but also a circulation method and a multi-stage treatment method as disclosed in Japanese Patent Laid-Open No. 7-328642 (incorporated herein by reference in its entirety).
- 43 The principle of electrolysis that may be effected as the step (A) will now be described while referring to FIG. 10. Incidentally, the description will be made of an ordinary case where TAA ions have OH ions as the counter ions.

- 44 As shown in FIG. 10, a cation exchange membrane 123 is disposed between a cathode 121 and an anode 122 to form a cathode cell (C) and an anode cell (D). In principle, the cation exchange membrane allows only cations to pass thereacross [actually, however, anions including photoresist (R.sup.-) and the like are slightly passed thereacross]. A starting solution (development waste or TAAH-containing solution derived therefrom) is passed through the anode cell (D), while (ultra)pure water, a solution of an electrolyte such as a low-concentration TAAH solution free of various impurities (e.g., a solution prepared by dissolving a small amount of virgin TAAH in pure or ultrapure water), or the like is passed as a concentrating liquid through the cathode cell (C). Since TAAH in the starting solution dissociates into TAA ions (TAA.sup.+) and OH ions (OH.sup.-), TAA ions as cations are transferred toward the cathode (-) to enter the cathode cell (C) across the cation exchange membrane 123 when a DC electric current is applied between the cathode 121 and the anode 122. On the cathode 121, hydrogen ions (H.sup.+) from water (H.sub.2O.rarw..fwdarw.H.sup.+ +OH.sup.-) receive electrons (e.sup.-) to generate hydrogen gas (H.sup.+), while residual OH ions (OH.sup.-) as anions become counter ions of TAA ions entering the cathode cell (C) from the anode cell (D) to form TAAH. Thus, TAAH is concentrated in the cathode cell (C) in keeping with progress of electrolysis. In this sense, the cathode cell (C) functions as a concentrating cell. On the other hand, on the anode 122, OH ions (OH.sup.-) of TAAH release electrons (e.sup.-) to become oxygen gas (O.sub.2) and water. In this sense, the anode cell (D) functions as a desalting cell wherein a desalted solution ("dilute solution" depleted of TAA ions) is formed.
- 45 The desalted solution obtained by electrolysis may be used as a source of photoresist as a surface-active substance either as such or after proper refining treatment thereof such as ion exchange resin treatment and/or chelate resin treatment.
- 46 Additionally stated, if ionic species such as Cl.sup.- or Br.sup.-, which is more liable to undergo electrolysis than OH.sup.-, is contained in the starting solution, a gas such as Cl.sub.2 or Br.sub.2 is generated. In this case, further division of the anode cell with an anion exchange membrane with addition of an alkaline substance such as ammonium hydroxide to a sectional cell on the anode's side can prevent generation of a gas such as Cl.sub.2 or Br.sub.2 through neutralization as disclosed in Japanese Patent Laid-Open No. 57-155390 published on Sep. 25, 1982 (incorporated herein by reference in its entirety). On the other hand, SO.sub.4.sup.2- and NO.sub.3.sup.- undergo electrolysis less easily than OH.sup.-, so that they remain in the form of H.sub.2SO.sub.4, HNO.sub.3, etc. with electrolysis of OH.sup.- involving generation of O.sub.2.
- 47 Two neutral membranes such as hydrophilized porous Teflon membranes may alternatively be used instead of the cation exchange membrane to provide an anode chamber, a middle chamber and a cathode chamber, wherein electrolysis can be effected by passing the starting solution through the middle chamber (Japanese Patent Laid-Open No. 60-247641 published on Dec. 7, 1985, incorporated herein by reference in its entirety).
- 48 When a higher-purity TAAH concentrate is desired to be obtained, a plurality of (preferably two) cation exchange membranes may be disposed between the cathode and the anode. In this case, the starting solution is passed through a cell on the anode's side (anode cell), while a concentrating liquid (liquid for recovery therein of TAAH) such for example as (ultra)pure water or a solution of an electrolyte such as a low-concentration TAAH solution free of various impurities (e.g., a solution prepared by dissolving a small amount of

virgin TAAH in pure or ultrapure water) is passed through a cell on the cathode's side (cathode cell) and the middle cell, whereby TAAH can be refined in multiple stages to obtain a high-purity TAAH concentrate from the cathode cell.

- 49 As for the electrodes used in the electrolysis, those made of the same materials as in the electrodialysis can be used. Examples of the electrolysis, which may be done batch-wise, semi-batch-wise or continuously, include a single-stage method, a circulation method, and a multi-stage treatment method as described before in connection with electrodialysis.
- 50 Additionally stated, the terms "concentrate" and "desalted solution" used herein are used to indicate whether the TAAH content is increased or decreased, and not to indicate which is higher or lower in TAAH concentration.
- 51 Examples of the anion exchange resin (desirably in the OH form) that may be used in the step (B) include styrene, acrylic or like type anion exchange resins in a fibrous, granular or like form, which are preferred in an aspect of treatment efficiency, and which may be used either alone or in the form of a mixture or a stratified structure of a plurality thereof at an arbitrary proportion. As described before, however, styrene type anion exchange resins are especially preferred in an aspect of photoresist removal efficiency. Incidentally, acrylic type anion exchange resins are those obtained by crosslinking (meth)acrylic acid and an ester(s) thereof with divinylbenzene (DVB) or the like. Strongly basic anion exchange resins are preferred in an aspect of photoresist removal efficiency although weakly basic anion exchange resins and medium base anion exchange resins can also be used.
- 52 Examples of the cation exchange resin in the H or TAA form that may be used in the step (B) include styrene, acrylic or like type cation exchange resins in a fibrous, granular or like form, which are preferred in an aspect of treatment efficiency, and which may be either weakly acidic or strongly acidic. They may be used either alone or in the form of a mixture or a stratified structure of a plurality thereof at an arbitrary proportion.
- 53 Commercially available cation exchange resins are usually in the H or Na form. Such a cation exchange resin (preferably converted into the H form if originally in the Na form) may preliminarily be converted into the TAA form before service thereof to prevent occurrence of a phenomenon that TAAH is adsorbed on the cation exchange resin in the initial stage of solution passage through the cation exchange resin to lower the TAAH concentration of the resultant treated solution. More specifically, a cation exchange resin is used preferably after converted into the TAA form though it can be used in the H form as it is. However, the cation exchange resin not completely in the TAA form but partially in the H form may also be used, or both of a cation exchange resin in the H form and a cation exchange resin in the TAA form may alternatively be used in the form of either a mixture or a stratified structure at an arbitrary proportion.
- 54 Use of either the anion exchange resin or the cation exchange resin alternately treated with an aqueous alkali solution and an aqueous acid solution and then well washed with (ultra)pure water is preferred in order to make it free from any matter that may be leached out therefrom during the service thereof.
- 55 Which one of an anion exchange resin and a cation exchange resin, or both to use as the ion exchange resin may be determined based on the permissible amounts of various impurities such as anions and cations that may remain in a

TAAH solution to be recovered in connection with a use of that solution. In the case where the recovered TAAH solution, after mixed with a surface-active substance, is used as a developer for use in production of electronic parts such for example as semiconductor devices, liquid crystal displays and printed boards as described before, however, both of the anion exchange resin and the cation exchange resin are desirably used.

- 56 When both of an anion exchange resin and a cation exchange resin are used as the ion exchange resin, the anion exchange resin and the cation exchange resin may be mixed with each other and used in the form of a mixed ion exchange resin packed in a column or a tower, but are preferably used in the form of a stratified structure packed in a column or a tower, wherein the anion exchange resin is disposed on the upstream side of the cation exchange resin disposed on the downstream side. When the development waste is preliminarily subjected to a multi-stage electrodialysis treatment or the like to make the concentrate have the photoresist remaining little, or when the original development waste contains only a slight amount of photoresist, however, the cation exchange resin may be disposed on the upstream side of the anion exchange resin disposed on the downstream side. An upstream column or tower packed with the anion exchange resin may alternatively be disposed separately from but used in connection with a downstream column or tower packed with the cation exchange resin. In this case, only one of the anion and cation exchange resins, when lowered in ion exchange capacity or deteriorated through long-time service, can conveniently be easily replaced with the virgin one. In the foregoing case of separate columns or towers, other treatment unit may be disposed between the two columns or towers.
- 57 An advantage involved in the case where the anion exchange resin is disposed on the upstream side of the cation exchange resin disposed on the downstream side is that, since it is conceivable that a trace amount of an amine may be leached out from the anion exchange resin, this leached-out amine, if any, can be trapped on the cation exchange resin disposed on the downstream side.
- 58 Examples of the NF membrane that may be used in the step (C) include NTR-7410, NTR-7450, NTR-725HF, NTR-7250, NTR-729HF, and NTR-769SR manufactured by NITTO DENKO CORPORATION; SU-200S, SU-500, and SU-600 manufactured by Toray Industries, Inc.; NF-45, NF-55, NF-70, and NF-90 manufactured by FilmTec Corporation; DESAL-5L and DESAL-5K manufactured by Desal Co. Limited; TS-80 manufactured by TrySep Corporation; TFC-S manufactured by Fluid Systems; and MPF-34, MPF-36, MPT-34, MPT-36, MPS-34 and MPS-36 of Sel RO (registered trademark) series manufactured by Koch Membrane Systems, Inc.
- 59 An NF membrane having a surface thereof charged negative is preferably used as a membrane principally aimed at separation and removal of photoresist into the concentrate. Since the photoresist usually exists in the anionic form in the development waste or the TAAH-containing treated solution derived therefrom [e.g., TAAH-containing solution treated in the step (A) and/or (B)], the use of the NF membrane having a surface thereof charged negative improves the rejection against the photoresist and hardly brings about fouling (contamination) of the NF membrane otherwise attributed to attachment thereto of the photoresist. In this case, an anionic surfactant, when contained in the development waste or the TAAH-containing treated solution derived therefrom, can also be effectively separated and removed into the concentrate. Further, in general, the NF membrane is also capable of separating and removing a nonionic surfactant, a cationic surfactant, etc. into the concentrate. Needless to say, an NF membrane having a surface thereof charged positive or a neutral NF membrane may also be used in accordance with properties of the development waste or the TAAH-containing treated solution derived therefrom (e.g., the kind of surfactant, if contained therein). The concentrate

containing the photoresist and/or a surfactant and thus separated with the NF membrane may be used as a source of surface-active substance either as such or after proper refining treatment thereof such as ion exchange resin treatment and/or chelate resin treatment if necessary.

- 60 In general, the NF membrane is comparatively weak against a high-pH solution. In order to prolong the life span of the NF membrane, the pH of a solution to be treated therewith is desired to be adjusted to a value of 9.5 to 12 if necessary, and preferably to a value of 9.5 to 11, to which the pH is, however, not limited in so far as the use of the NF membrane is well costeffective. It is preferred to provide a safety filter of at most 25 .mu.m in pore size in front of the NF membrane in order to avoid a fear of clogging of the NF membrane with fine impurity particles and the like. This applies at whatever stage the step (C) of separation with the NF membrane is taken. Care must also be taken because the increasing TAAH concentration of the solution being treated with the NF membrane raises the operating pressure of a nanofilter and shortens the life span of the NF membrane with an increase in pH.
- 61 When a large amount of TAAH is still contained in the concentrate obtained in the step (C), a variety of refining step(s) for improving the TAAH recovery may be taken at a later stage(s), whereby the concentrate can be refined either to some degree of purification commensurate with the application of the rejuvenated developer or to such a high degree of purification that the rejuvenated developer can be reused in electronic part production processes and the like as the case may be.
- 62 Since the permeate obtained in the step (C) (hereinafter often referred to as the "NF permeate") is a TAAH solution having a considerably high purity, it may advantageously be passed as a concentrating liquid (liquid for recovery therein of TAAH) through the concentrating cell(s) of an electrodialysis or electrolysis unit, while the concentrate obtained in the step (C) (hereinafter often referred to as the "NF concentrate") may be passed as a starting solution (solution to be depleted of TAAH) through the desalting cell(s) of the electrodialysis or electrolysis unit, if the NF concentrate contains a considerable amount of TAAH remaining therein (Japanese Patent Laid-Open No. 11-192481). In this case, since the NF permeate is used instead of (ultra)pure water as the concentrating liquid, the amount of wastewater discharged as desalted waste can advantageously be decreased. Further, the amount of TAAH to be transferred into the concentrating liquid by electrodialysis or electrolysis can advantageously be decreased to reduce the running cost and miniaturize the unit. When the wastewater discharged as desalted waste from the electrodialysis or electrolysis unit is a solution having a high photoresist and/or surfactant concentration, it may be used as a source of surface-active substance either as such or after a proper refining step as described above if necessary.
- 63 For example, when a refining step(s) such as the ion exchange treatment, electrodialysis and/or electrolysis step is taken, it is preferred that such a step(s) be taken after the step (C) of separation with the NF membrane, if taken, rather than before the step (C) from the standpoint of decreasing the load on a refining unit(s) for use in such a refining step(s) because the purity of the NF permeate is considerably high. For example, in the case where the step (C) is aimed at removing a slight amount of impurities (particularly some metal components including Fe and Al, and silica, which are hard to remove by ion exchange treatment, and the like), however, the refining step(s) such as the ion exchange treatment, electrodialysis and/or electrolysis step may be taken before the step (C). Needless to say, such refining steps may optionally be taken both before and after the step (C). In the case where the

impurity concentration of the original development waste is low, in the case where the use of the rejuvenated developer is such that a low purity thereof is tolerable, or in the like case, the NF permeate may alternatively be subjected to at least one of evaporation, reverse osmosis membrane treatment, electrodialysis and electrolysis for concentration of TAMH, and/or to adjustment of the TAAH concentration by addition thereto of a virgin conc. TAAH solution, or the like after the step (C) without ion exchange treatment.

- 64 Examples of the chelate resin usable in the chelate resin treatment step include iminodiacetic acid type, iminopropionic acid type, aminophosphonic acid type (e.g., aminomethylenephosphonic acid type), polyamine type, glucamine type (e.g., N-methylglucamine type), aminocarboxylic acid type, dithiocarbamic acid type, thiol type, amidoxime type, and pyridine type chelate resins, among which iminodiacetic acid type, iminopropionic acid type, aminomethylenephosphonic acid type, polyamine type, N-methylglucamine type chelate resins are preferred. An example of the iminodiacetic acid type chelate resins is AMBERLITE (registered trademark) IRC-718 manufactured by Rohm and Haas Company, an example of the iminopropionic acid type chelate resins is EPOROUS MX-8 manufactured by Miyoshi Oil & Fat Co., Ltd., an example of the aminomethylenephosphonic acid type chelate resins is DUOLITE (registered trademark) C-467 manufactured by Rohm and Haas Company, examples of the polyamine type chelate resins include SUMICHELATE (registered trademark) MC-10 manufactured by Sumitomo Chemical Co., Ltd. and DIAION (registered trademark) CR-20 manufactured by Mitsubishi Chemical Corporation, and an example of the N-methylglucamine type chelate resins is AMBERLITE IRA-743 manufactured by Rohm and Haas Company.
- 65 A trace amount of impurities, which pose a problem when the rejuvenated developer is reused, is polyvalent metallic ions [Fe(II), Fe(III), Al(III), etc.]. Since the chelate resin is highly selective for polyvalent metallic ions, treatment of contacting the chelate resin with the development waste or a TAAH-containing solution derived therefrom can effectively remove such polyvalent metallic ions. The chelate resin may also be used for the purpose of removing the above-mentioned polyvalent metallic ions from a photoresist-containing solution such as the development waste or a photoresist-containing treated solution derived therefrom, which may be used as a source of surface-active substance. The used chelate resin is regenerated for its reuse by treating the chelate resin with an acid such as hydrochloric acid for formation of a chelate resin in the H form and washing away the acid with (ultra)pure water, and preferably converting it into a chelate resin in the TAA form with an aqueous TAAH solution.
- 66 In an aspect of removal of impurities, it is preferred to use the chelate resin in combination with the ion exchange resin. The chelate resin may be used either before or after use of the ion exchange resin, and they may be used in the form of either single beds (separate beds) or a mixed bed. Any combination of chelate resin+anion exchange resin, chelate resin+anion exchange resin+cation exchange resin or chelate resin+cation exchange resin will suffice for the purpose of heightening the purity of a recovered TAAH solution. A combination of chelate resin+cation exchange resin is preferred for the purpose of heightening the purity of a photoresist-containing solution as a source of surface-active substance. Incidentally, in combining the chelate resin with both kinds of ion exchange resins, the order thereof may be anion exchange resin (cation exchange resin).fwdarw.chelate resin.fwdarw.cation exchange resin (anion exchange resin).
- 67 When the chelate resin and the ion exchange resin are used for heightening the purity of a TAAH solution in the course of obtaining the rejuvenated developer, use of an NF membrane in advance thereof is preferred in order to

lower the load on the chelate resin and the ion exchange resin. An NF membrane may be used after use of the chelate resin and the ion exchange resin for the purpose of further heightening the purity of a TAAH solution.

- 68 In equipment (system) for carrying out the present invention, water tanks provided if necessary and aimed at storing or retaining any solutions containing at least TAAH are preferably constructed in such a way that they are purged with an inert gas such as nitrogen gas or argon gas (Japanese Patent Laid-Open No. 10-165933 published on Jun. 23, 1998, incorporated herein by reference in its entirety). In this case, the water tanks are more preferably constructed in such a way that the inert gas pressure therein can be maintained higher than the atmospheric pressure, and especially preferably constructed in such a way that a water-sealing unit is attached to each of the water tanks purged with the inert gas. These provisions prevent strongly alkaline TAAH (TAA.sup.+ OH.sup.-) from being converted into a tetraalkylammonium hydrogencarbonate (TAA.sup.+ HCO.sub.3.sup.-) and/or a tetraalkylammonium carbonate [(TAA.sup.+).sub.2 CO.sub.3.sup.2-] due otherwise to dissolution of carbon dioxide gas (CO.sub.2) in the atmosphere into a TAAH-containing solution through contact therebetween, and prevent other impurities in the atmosphere (various gases such as acidic gases other than CO.sub.2 and oxidizing gases, dust, dirt, metals, salts, etc.) from mixing in that solution. When the development waste or a photoresist-containing treated solution derived therefrom is used as a source of surface-active substance to be added to the recovered TAAH solution, the same measure is preferably taken for the purpose of preventing impurities in the atmosphere from mixing therein. This is particularly desired when the rejuvenated developer is to be used as a developer for use in production of electronic parts such as semiconductor devices.
- 69 If necessary, an analytical controller(s) including a quantitative determination apparatus for the photoresist concentration of the development waste and/or a variety of TAAH-containing treated solution or photoresist-containing treated solution thereof [e.g., absorption spectrometer, or (ultraviolet-visible light) absorptiometer], and, if necessary, a quantitative determination apparatus for the TAAH concentration thereof (e.g., pH-metric titrating apparatus, potentiometric titrating apparatus, conductivity meter, or ultrasonic concentration meter) may favorably be provided at a suitable position(s) in equipment (system) for carrying out the process of the present invention (Japanese Patent Laid-Open No. 10-207082 published on Aug. 7, 1998, incorporated herein by reference in its entirety). If further necessary, a temperature controller(s) having at least a cooling function may be provided at a suitable position(s), while a TAAH concentration controller may be provided around the terminal of the system favorably to enable the resultant rejuvenated developer to be fed directly to a development unit (Japanese Patent Laid-Open No. 11-128691 published on May 18, 1999, incorporated herein by reference in its entirety).
- 70 When a suitable amount of TAAH and/or (ultra)pure water is added to the recovered TAAH solution before service of it as a rejuvenated developer in the development step, use can be made of a TAAH concentration determination apparatus such for example as a pH-metric titrating apparatus, a potentiometric titrating apparatus, a conductivity meter or an ultrasonic concentration meter, preferably a conductivity meter or an ultrasonic concentration meter. Incidentally, the conductivity meter makes the most of the fact that the TAAH concentration can be measured in dominantly linear correlation thereof with the conductivity around the serviceable TAAH concentration. On the other hand, the ultrasonic concentration meter is a determination apparatus whereby the concentration of a solution is found through measurement of ultrasonic wave propagation rate and temperature by

making the most of the facts that the ultrasonic wave propagation rate through the solution, and the density and bulk modulus of the solution have a fundamental relation, and that the bulk modulus and density of the solution depend on the concentration and temperature of the solution.

- 71 A membrane treatment unit may further be provided at or near the terminal of the system for carrying out the present invention. In this case, fine particles that exist in the development waste from the beginning, and fine particles that may mix therein from pumps, an electrodialysis and/or electrolysis unit, a chelate resin, an ion exchange resin, etc., if any, can favorably be removed for certain. This may be applicable either to the recovered TAAH solution or to the photoresist-containing treated solution, but is preferably applied to the rejuvenated developer before it is sent to the development step.
- 72 Examples of such a membrane treatment unit include a microfiltration membrane unit wherein use is made of a polyethylene (PE), polypropylene (PP) or polytetrafluoroethylene (PTFE) membrane filter having micropores of about 0.03 to 1 μm in diameter, and an ultrafiltration membrane unit. A suitable membrane treatment unit may be chosen and used in accordance with the purpose of treatment. A nanofilter may alternatively be used instead of the above-mentioned membrane treatment units.
- 73 According to the present invention, as a suitable example of equipment for performing the process of the present invention, there is provided equipment for recovering a developer from a photoresist development waste and reusing it; characterized by comprising a recovery and refining unit for separating impurities including photoresist from a photoresist development waste to recover a tetraalkylammonium hydroxide solution, and a rejuvenated developer adjustment unit for mixing the tetraalkylammonium hydroxide solution recovered from the recovery and refining unit with part of the photoresist development waste preferably treated with a cation exchange resin and/or chelate resin treatment unit and/or at least part of a photoresist-containing waste recovered from the recovery and refining unit and preferably treated with a cation exchange resin and/or chelate resin treatment unit, and optionally replenishing them with (ultra)pure water and/or tetraalkylammonium hydroxide as needed to obtain a rejuvenated developer, which is fed to a development unit. Herein, the "recovery and refining unit" comprises at least one of units for use in various steps as mentioned hereinabove in connection with the method of separating impurities such as photoresist from a development waste to recover a TAAH solution. Using this developer recovery and reuse equipment, a developer can be recirculated and reused in a factory.
- 74 This developer recovery and reuse equipment desirably further comprises a circulation line attached to the rejuvenated developer adjustment unit and provided with a photoresist concentration determination apparatus for the rejuvenated developer and a TAAH concentration determination apparatus for the rejuvenated developer, and a controller for controlling to desired values the flow rates of the recovered TAAH solution, part of the photoresist development waste preferably treated with the cation exchange resin and/or chelate resin treatment unit and/or at least part of the photoresist-containing waste recovered from the recovery and refining unit and preferably treated with the cation exchange resin and/or chelate resin treatment unit, and (ultra)pure water and/or TAAH (aqueous solution) through operation of the measured values of photoresist concentration and TAAH concentration as input data. This enables automatic recirculation and reuse of the developer in a factory.
- 75 According to the present invention, as another suitable example of equipment for performing the process of the present invention, there is provided

equipment for recovering a developer from a photoresist development waste and reusing it; characterized by comprising a recovery and refining unit for separating impurities including photoresist from the photoresist development waste to recover a tetraalkylammonium hydroxide solution, a first rejuvenated developer adjustment unit for replenishing the recovered tetraalkylammonium hydroxide solution with (ultra)pure water and/or tetraalkylammonium hydroxide as needed to obtain a first rejuvenated developer having a desired tetraalkylammonium hydroxide concentration, a second rejuvenated developer adjustment unit for replenishing part of the photoresist development waste preferably treated with a cation exchange resin and/or chelate resin treatment unit and/or at least part of a photoresist-containing waste recovered from the recovery and refining unit and preferably treated with a cation exchange resin and/or chelate resin treatment unit with (ultra)pure water and/or tetraalkylammonium hydroxide as needed to obtain a second rejuvenated developer having a desired tetraalkylammonium hydroxide concentration, and a mixer for mixing the first rejuvenated developer with the second rejuvenated developer to prepare a mixed rejuvenated developer, which is fed to a development unit. Herein, the "recovery and refining unit" comprises at least one of units for use in various steps as mentioned hereinbefore in connection with the method of separating impurities such as photoresist from a development waste to recover a TAAH solution. Using this developer recovery and reuse equipment, a developer can be recirculated and reused in a factory.

- 76 This developer recovery and reuse equipment desirably further comprises flow meters for measuring the respective flow rates of the first and second rejuvenated developers, a photoresist concentration determination apparatus for the second rejuvenated developer, a photoresist concentration determination apparatus for the mixed rejuvenated developer, and a controller for controlling the respective flow rates of the first and second rejuvenated developers in such a manner that the photoresist concentration of the mixed rejuvenated developer becomes a desired value through operation of the measured values of flow rates and photoresist concentrations as input data. This enables automatic recirculation and reuse of the developer in a factory.
- 77 According to the present invention, as a suitable simple example of equipment for performing the process of the present invention, there is provided equipment for recovering a developer from a photoresist development waste and reusing it; characterized by comprising a rejuvenated developer adjustment unit comprising a development waste storage and rejuvenated developer adjustment tank, and a recovery and refining unit for separating impurities including photoresist from a solution sent from the development waste storage and rejuvenated developer adjustment tank to recover a tetraalkylammonium hydroxide solution, which is sent back to the development waste storage and rejuvenated developer adjustment tank and mixed with the solution in the development waste storage and rejuvenated developer adjustment tank, and optionally replenished with (ultra)pure water and/or tetraalkylammonium hydroxide as needed to prepare a rejuvenated developer, which is fed to a development unit. Herein, the "refining and recovery unit" comprises at least one of units for use in various steps as mentioned hereinbefore in connection with the method of separating impurities such as photoresist from the development waste to recover a TAAH solution. Using this developer recovery and reuse equipment, a developer can be recirculated and reused in a factory.
- 78 This developer recovery and reuse equipment desirably further comprises a circulation line attached to the rejuvenated developer adjustment unit and provided with a photoresist concentration determination apparatus for the solution in the development waste storage and rejuvenated developer adjustment tank and a TAAH concentration determination apparatus for the solution in the development waste storage and rejuvenated developer adjustment tank, and a

controller for controlling to desired values the respective flow rates of at least part of the photoresist development waste preferably treated with a cation exchange resin and/or chelate resin treatment unit and the tetraalkylammonium hydroxide solution, and optionally at least part of a photoresist-containing waste recovered from the recovery and refining unit and preferably treated with a cation exchange resin and/or chelate resin treatment unit, and further optionally (ultra)pure water and/or TAAH (aqueous solution) through operation of the measured values of photoresist concentration and TAAH concentration as input data. This enables automatic recirculation and reuse of the developer in a factory.

DRAWING DESCRIPTION:

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing objects, features and advantages of the present invention will be better understood from the following description taken in connection with the accompanying drawings, in which:

FIG. 1 is a block diagram of an example of basic equipment for carrying out the present invention;

FIG. 2 is a block diagram of another example of basic equipment for carrying out the present invention;

FIG. 3 is a block diagram of still another example of basic equipment for carrying out the present invention;

FIG. 4 is a block diagram of a further example of basic equipment for carrying out the present invention;

FIG. 5 is a flow diagram illustrating the constitution of an example of rejuvenated developer adjustment unit including a rejuvenated developer adjustment tank that may be used in carrying out the present invention;

FIG. 6 is a flow diagram illustrating the constitution of an example of rejuvenated developer adjustment unit including a mixer for rejuvenated developer adjustment that may be used in carrying out the present invention;

FIG. 7 is a block diagram of an example of basic and simple equipment for carrying out the present invention;

FIG. 8 is a flow diagram illustrating an automatized example of the basic equipment of FIG. 7;

FIG. 9 is an illustration showing the principle of electrodialysis that may be done in the process of the present invention; and

FIG. 10 is an illustration showing the principle of electrolysis that may be done in the process of the present invention.

DETAILED DESCRIPTION:

1 PREFERRED MODES FOR CARRYING OUT THE INVENTION

2 Preferred modes for carrying out the present invention will now be described while referring to FIGS. 1 to 8, but should not be construed as limiting the scope of the present invention. Additionally stated, in the following figures,

the "TAAH recovery and refining unit" comprises a variety of unit(s) such as an electrodialysis unit and/or an electrolysis unit, an ion exchange treatment unit, a nanofilter, a chelate resin treatment unit, and/or the like, incorporated thereinto in accordance with the purpose.

- 3 FIG. 1 is a block diagram of an example of basic equipment for carrying out the present invention. A development waste from a development unit is once stored in a development waste tank if necessary, and then sent to a TAAH recovery and refining unit to obtain a recovered refined TAAH solution, which is then sent to a rejuvenated developer adjustment unit, wherein the TAAH solution is then mixed with a surface-active substance such as a surfactant, and replenished and mixed with (ultra)pure water and/or TAAH (aqueous solution) as needed for adjustment of its surface-active substance concentration and TAAH concentration to obtain a rejuvenated developer, which is then sent to the development unit, wherein it is reused in the development step. Incidentally, virgin TAAH (aqueous solution) is usually used for replenishment, but a TAAH solution recovered and refined in any other step may instead be used. The excess waste (desalted solution in electrodialysis or electrolysis, NF concentrate in NF membrane treatment, or the like) from the TAAH recovery and refining unit is discharged as wastewater via a wastewater line sometimes together with the excess development waste from the development waste tank.
- 4 FIG. 2 is a block diagram of another example of basic equipment for carrying out the present invention. A development waste from a development unit is once stored in a development waste tank if necessary, and part of it is then sent to a TAAH recovery and refining unit to obtain a recovered refined TAAH solution while sending other part of it to a photoresist-containing solution tank. If necessary, that other part of the development waste is mixed with at least part of a photoresist-containing waste (desalted solution in electrodialysis or electrolysis, NF concentrate in NF membrane treatment, or the like) recovered from the TAAH recovery and refining unit. Only the development waste or only the photoresist-containing waste recovered from the TAAH recovery and refining unit may alternatively be sent to the photoresist-containing solution tank. The photoresist-containing solution from the photoresist-containing solution tank is sent as a source of photoresist as a surface-active substance to a rejuvenated developer adjustment unit preferably via a cation exchange resin and/or chelate resin treatment unit, and then mixed there with the recovered refined TAAH solution from the TAAH recovery and refining unit, and replenished with (ultra)pure water and/or TAAH (aqueous solution) as needed for adjustment of the photoresist concentration and TAAH concentration of the mixture to obtain a rejuvenated developer, which is then sent to the development unit, wherein it is reused in the development step.
- 5 In FIG. 2, the "photoresist-containing solution tank" is provided if necessary, and may be dispensed with. Where the photoresist-containing solution tank is dispensed with, the development waste in the development waste tank or the waste recovered from the TAAH recovery and refining unit may be sent to the rejuvenated developer adjustment unit either directly or via the cation exchange resin and/or chelate resin treatment unit. Virgin TAAH (aqueous solution) is usually used for replenishment, but a TAAH solution recovered and refined in any other step may instead be used. The excess waste (desalted solution in electrodialysis or electrolysis, NF concentrate in NF membrane treatment, or the like) from the TAAH recovery and refining unit is discharged as wastewater via a wastewater line sometimes together with the excess development waste from the development waste tank and/or the excess photoresist-containing solution from the photoresist-containing solution tank.
- 6 FIG. 3 is a block diagram of still another example of basic equipment for

carrying out the present invention. A development waste from a development unit is once stored in a development waste tank if necessary, and then sent to a TAAH recovery and refining unit to obtain a recovered refined TAAH solution, which is then sent to a rejuvenated developer adjustment unit, wherein the solution is replenished and mixed with (ultra)pure water and/or TAAH (aqueous solution) as needed for adjustment of its TAAH concentration to a desired one (about 2.4 wt. % in the case of TMAH) to obtain a rejuvenated developer. On the other hand, (ultra)pure water and TAAH (aqueous solution) are mixed with a surface-active substance such as a surfactant in a developer adjustment unit to obtain a virgin developer having its TAAH concentration adjusted to a desired one (about 2.4 wt. % in the case of TMAH). The rejuvenated developer and the virgin developer are sent to a mixer, wherein they are mixed to obtain an adjusted developer having a desired surface-active substance concentration, which is then sent to a development unit, wherein it is used in the development step. Virgin TAAH (aqueous solution) is usually used for replenishment, but a TAAH solution recovered and refined in any other step may instead be used. The excess waste (desalted solution in electrodialysis or electrolysis, NF concentrate in NF membrane treatment, or the like) from the TAAH recovery and refining unit is discharged as wastewater via a wastewater line sometimes together with the excess development waste from the development waste tank.

7 FIG. 4 is a block diagram of a further example of basic equipment for carrying out the present invention. A development waste from a development unit is once stored in a development waste tank if necessary, and part of it is then sent to a TAAH recovery and refining unit while sending other part of it to a photoresist-containing solution tank. If necessary, that other part of the development waste is mixed with at least part of a photoresist-containing waste (desalted solution in electrodialysis or electrolysis, NF concentrate in NF membrane treatment, or the like) recovered from the TAAH recovery and refining unit. Only the development waste or only the photoresist-containing waste recovered from the TAAH recovery and refining unit may alternatively be sent to the photoresist-containing solution tank. The photoresist-containing solution from the photoresist-containing solution tank is sent as a source of photoresist as a surface-active substance to a second rejuvenated developer adjustment unit preferably via a cation exchange resin and/or chelate resin treatment unit, and replenished and mixed with (ultra)pure water and/or TAAH (aqueous solution) as needed for adjustment of its TAAH concentration to a desired one (about 2.4 wt. % in the case of TMAH) to obtain a second rejuvenated developer containing the photoresist. On the other hand, a recovered refined TAAH solution obtained from the TAAH recovery and refining unit is sent to a first rejuvenated developer adjustment unit, wherein it is then replenished and mixed with (ultra)pure water and/or TAAH (aqueous solution) as needed for adjustment of its TAAH concentration to a desired one (about 2.4 wt. % in the case of TMAH) to obtain a first rejuvenated developer. The first and second rejuvenated developers are sent to a mixer, wherein they are then mixed to obtain a mixed rejuvenated developer having a desired photoresist concentration, which is then sent to a development unit, wherein it is reused in the development step. Incidentally, the photoresist-containing solution tank is provided if necessary, and may be dispensed with like in FIG. 2. Virgin TAAH (aqueous solution) is usually used for replenishment, but a TAAH solution recovered and refined in any other step may instead be used. The excess waste (desalted solution in electrodialysis or electrolysis, NF concentrate in NF membrane treatment, or the like) from the TAAH recovery and refining unit is discharged as wastewater via a wastewater line sometimes together with the excess development waste from the development waste tank and/or the excess photoresist-containing solution from the photoresist-containing solution tank.

- 8 FIG. 5 is a flow diagram illustrating the constitution of an example of rejuvenated developer adjustment unit including a rejuvenated developer adjustment tank that may be used in carrying out the present invention. This unit can favorably be incorporated into, e.g., the basic equipment (system) of FIG. 2. A recovered and refined TAAH-containing solution, a photoresist-containing solution preferably treated with a cation exchange resin and/or a chelate resin, (ultra)pure water, and TAAH (aqueous solution) are fed via respective automatic control valves V to the rejuvenated developer adjustment tank, which is provided with a level sensor LS for detecting the level of the solution surface. A circulation line equipped with a photoresist concentration determination apparatus A such as an absorptiometer and a TAAH concentration determination apparatus B such as a conductivity meter or an ultrasonic concentration meter is attached to the rejuvenated developer adjustment tank to measure the photoresist and TAAH concentrations of the rejuvenated developer in the rejuvenated developer adjustment tank. This circulation line may have a function of agitating the rejuvenated developer. The detected value of the level of the solution surface, and the measured values of the photoresist and TAAH concentrations are inputted to a controller. Based on the inputted values, the controller outputs signals for controlling the respective automatic control valves V and pumps P. In FIG. 5, control lines are expressed by broken lines. The rejuvenated developer thus adjusted is once sent to and stored in a developer tank if necessary, and then sent to a development unit for reuse thereof.
- 9 FIG. 6 is a flow diagram illustrating the constitution of an example of rejuvenated developer adjustment unit including a mixer for rejuvenated developer adjustment that may be used in carrying out the present invention. This unit can favorably be incorporated into, e.g., the basic equipment (system) of FIG. 4. The mixer is fed via respective automatic control valves V with a recovered refined solution (corresponding to the first rejuvenated developer in the description of FIG. 4) adjusted to a desired TAAH concentration (about 2.4 wt. % in the case of TMAH), and a photoresist-containing TAAH solution (corresponding to the second rejuvenated developer in the description of FIG. 4) adjusted to a desired TAAH concentration (about 2.4 wt. % in the case of TMAH) by adding (ultra)pure water and TAAH (aqueous solution) as needed to a photoresist-containing solution preferably treated with a cation exchange resin and/or a chelate resin. The photoresist concentration and flow rate of the adjusted photoresist-containing TAAH solution are measured with a photoresist concentration determination apparatus A1 such as an absorptiometer and a flow indicator FI-1 to input the measured values to a controller. On the other hand, the flow rate of the adjusted recovered refined solution is measured with a flow indicator FI-2 to input the measured value to the controller. The photoresist concentration of the rejuvenated developer obtained from the mixer is measured with a photoresist concentration determination apparatus A2 such as an absorptiometer to input the measured value to the controller. The controller, to which the measured values have been inputted, controls flow rate control valves V respectively attached to an adjusted recovered refined solution line and an adjusted photoresist-containing TAAH solution line to control the photoresist concentration of the rejuvenated developer to a desired value. In FIG. 6, control lines are expressed by broken lines, and a pump is denoted by P. The rejuvenated developer thus adjusted is once sent to and stored in a developer tank if necessary, and sent to a development unit for reuse thereof.
- 10 Incidentally, although a pump is used as a means for sending the developer from the developer tank to the development unit in the foregoing embodiments of FIGS. 5 and 6, the developer tank may alternatively be pressurized with N.sub.2 gas or the like to send the developer without using the pump. In FIGS.

5 and 6, the developer tank is provided if necessary, and may be dispensed with.

- 11 FIG. 7 is a block diagram of an example of basic simple equipment for carrying out the present invention. At least part of a development waste from a development unit is sent to the development waste storage and rejuvenated developer adjustment tank of a rejuvenated developer adjustment unit, from which part of the solution is sent to a TAAH recovery and refining unit. In passing, when an excess of development waste is generated, or when the development waste has a low TAAH concentration, it may be directly discharged as wastewater via a wastewater line, which is, however, not always necessary. A recovered and refined TAAH solution from the TAAH recovery and refining unit may be returned back to the development waste storage and rejuvenated developer adjustment tank, which is supplied with (ultra)pure water and/or TAAH (aqueous solution) as needed for photoresist and TAAH concentrations adjustment to adjust the solution in the tank to a rejuvenated developer, which is then sent to the development unit, wherein it is reused in the development step. At least part of the photoresist-containing waste (e.g., desalted solution in electrodialysis or electrolysis, NF concentrate in NF membrane treatment, or the like) recovered from the TAAH recovery and refining unit may be returned back to the development waste storage and rejuvenated developer adjustment tank preferably via a cation exchange resin and/or chelate resin treatment unit (not shown in the figure). Since the photoresist-containing development waste as a source of surface-active substance flows directly into the development waste storage and rejuvenated developer adjustment tank, however, the foregoing mode may not necessarily be adopted, and the photoresist-containing waste recovered from the TAAH recovery and refining unit may simply be discharged as wastewater via a wastewater line. At a necessary time or if necessary, the excess solution from the development waste storage and rejuvenated developer adjustment tank may be discharged as wastewater via the wastewater line.
- 12 FIG. 8 is a flow diagram illustrating an automatized example of the basic equipment of FIG. 7. In the equipment of FIG. 8, a development waste storage and rejuvenated developer adjustment tank is fed with a development waste, a recovered refined TAAH-containing solution, (ultra)pure water and TAAH (aqueous solution) via respective automatic control valves V. If necessary, a photoresist-containing waste recovered from a TAAH recovery and refining unit and preferably treated with a cation exchange resin and/or a chelate resin (not shown in the figure) may be returned back to the development waste storage and rejuvenated developer adjustment tank via an automatic control valve V for it. The development waste storage and rejuvenated developer adjustment tank is provided with a level sensor LS for detecting the level of the solution surface. A circulation line equipped with a photoresist concentration determination apparatus C such as an absorptiometer and a TAAH concentration determination apparatus D such as a conductivity meter or an ultrasonic concentration meter is attached to the development waste storage and rejuvenated developer adjustment tank to measure the photoresist and TAAH concentrations of the solution in the development waste storage and rejuvenated developer adjustment tank. This circulation line may have a function of agitating the rejuvenated developer. The detected value of the level of the solution surface, and the measured values of the photoresist and TAAH concentrations are inputted to a controller. Based on the inputted values, the controller outputs signals for controlling the respective automatic control valves V and pumps P. In FIG. 8, control lines are expressed by broken lines. Any redundant explanations are dispensed with because others are the same as described in connection with FIG. 7.

13 EXAMPLES

- 14 The following Examples will specifically illustrate the present invention, but should not be construed as limiting the scope of the present invention. In the following Examples, the TMAH concentration was analyzed according to ion-exchange chromatography, the photoresist concentration was measured according to absorptiometry while using an ultraviolet-visible light absorptiometer [the measured absorbance at 290 nm (absorption being assigned to photoresist) was mentioned as such], and the Na concentration was measured according to atomic absorption spectrometry.
- 15 Example 1
- 16 TMAH was recovered and refined with an electrodialyzer and an ion exchange treatment unit (mixed bed) from a photoresist development waste discharged from an LCD production process. The water quality of this development waste involved a TMAH concentration of 8,600 mg/l, an absorbance at 290 nm of 3.48 and an Na concentration of 510 .mu.g/l.
- 17 TMAH in this development waste as a starting solution was separated, concentrated and recovered into ultrapure water (concentrating liquid) with the electrodialyzer according to a circulation method to obtain a recovered solution. MICRO ACILYZER (registered trademark) G3 manufactured by Asahi Chemical Industry Co., Ltd. was used as the electrodialyzer, wherein use was made of cation exchange membranes ACIPLEX K-501 manufactured by Asahi Chemical Industry Co., Ltd., neutral membranes ACIPLEX PVA #100 manufactured by Asahi Chemical Industry Co., Ltd. instead of anion exchange membranes, and platinum-plated titanium electrodes as both the anode and the cathode.
- 18 The recovered solution was then passed through a column packed, in the form of a mixed bed, with a cation exchange resin AMBERLITE 200C (manufactured by Rohm and Haas Company) preliminarily converted into the TMA form (tetramethylammonium ion form) by passing therethrough a virgin aqueous TMAH solution and a strongly basic anion exchange resin AMBERLITE IRA-900 (manufactured by Rohm and Haas Company) in the OH form, whereby it was refined to obtain a TMAH solution having a TMAH concentration of 22,700 ppm, an absorbance at 290 nm of less than 0.01, and an Na concentration of less than 10 ppb, to which a semiconductor grade 25 wt. % TMAH reagent containing no surfactants was then added to obtain a TMAH concentration-adjusted solution having a TMAH concentration of 23,800 ppm, an absorbance at 290 nm of less than 0.01, and an Na concentration of less than 10 ppb.
- 19 On the other hand, the development waste was passed through a column packed with a cation exchange resin AMBERLITE 200C preliminarily converted into the TMA form to effect ion exchange treatment, and then admixed with a semiconductor grade 25 wt. % TMAH reagent containing no surfactants to obtain a photoresist-containing treated solution having a TMAH concentration of 23,800 ppm, an absorbance at 290 nm of 3.25, and an Na concentration of less than 10 ppb.
- 20 The TMAH concentration-adjusted solution and the photoresist-containing treated solution, obtained by the foregoing respective procedures, were mixed with each other at a proper proportion to obtain a photoresist concentration-adjusted mixed solution.
- 21 Each of a virgin TMAH solution containing no surfactants, the TMAH concentration-adjusted solution and the photoresist concentration-adjusted adjusted mixed solution was dropped on a photoresist coating film formed on a glass plate to measure the contact angle therebetween one minute after

dropping. The results are shown in Table 1, wherein "Virgin Solution" refers to the virgin TMAH solution, "Adjusted Solution" to the TMAH concentration-adjusted solution, "Mixed Solution" to the photoresist concentration-adjusted mixed solution, "TMAH" to the TMAH wt. percentage, and "Absorbance" to a value of absorbance measured at 290 nm using the ultraviolet-visible light absorptiometer.

TABLE 1

Solution	TMAH	Absorbance	Contact Angle (.degree.)
Mixed Solution 1	2.38	3.0	35
Mixed Solution 2	2.38	2.0	37
Adjusted Solution	2.38	0.0	39
Virgin Solution	2.38	0.0	39

- 22 Table 1 demonstrates that the higher the photoresist concentration (the higher the absorbance at 290 nm), the lower the contact angle of the mixed solution (rejuvenated developer) with the photoresist coating film, because the dissolved photoresist contained in the development waste had a surface-active effect. This makes it understandable that a rejuvenated developer having an arbitrary surface tension can be obtained by adding the photoresist as a surface-active substance to a recovered TMAH solution to adjust the photoresist concentration thereof.
- 23 According to the present invention, a surface-active substance such as a surfactant or a dissolved photoresist contained in a development waste is mixed with a TAAH solution recovered from the development waste to properly adjust the surface-active substance concentration thereof, whereby a rejuvenated developer having an arbitrary surface tension can be obtained. Thus, a rejuvenated developer suitable for a variety of development step can be recovered from a development waste, and reused therein.
- 24 In rejuvenation treatment of a photoresist development waste for the purpose of obtaining a rejuvenated developer for use in production of, e.g., electronic parts such as semiconductor devices, liquid crystal displays or printed boards, wherein impurities must particularly be avoided, refining treatment steps such as NF membrane separation treatment, electrodialysis and/or electrolysis, ion exchange treatment, and chelate resin contact treatment steps may be properly combined to recover a TAAH solution, which is then mixed with a source of surface-active substance such as a surfactant, a development waste, a photoresist-containing treated solution thereof obtained in NF membrane separation treatment, electrodialysis and/or electrolysis or the like step, or a refined photoresist-containing solution thereof obtained through any refining treatment as needed, whereby a rejuvenated developer having a desired surface tension can be recovered and reused in the development step.
- 25 The entire disclosure of Japanese Patent Application No. 10-309606 filed on Oct. 30, 1998 including specification, claims, drawings and summary is incorporated herein by reference in its entirety.

CLAIMS:

What is claimed is:

1. Equipment for recovering a developer from a photoresist development waste and reusing it; comprising a source of photoresist development waste including tetraalkylammonium hydroxide; a recovery and refining unit for separating impurities including photoresist from a photoresist development waste to recover tetraalkylammonium hydroxide solution, a rejuvenated developer adjustment unit operable for mixing said tetraalkylammonium hydroxide solution recovered from said recovery and refining unit with at least one of part of the photoresist development waste and at least part of a photoresist-containing waste recovered from said recovery and refining unit to obtain a rejuvenated developer, and a development unit arranged to be fed with said rejuvenated developer.
2. Equipment for recovering a developer from a photoresist development waste and reusing it as claimed in claim 1; which further comprises a circulation line attached to said rejuvenated developer adjustment unit and provided with a photoresist concentration determination apparatus for the rejuvenated developer and a tetraalkylammonium hydroxide concentration determination apparatus for the rejuvenated developer, and a controller for controlling to desired values the flow rates of the recovered tetraalkylammonium hydroxide solution, at least one of part of the photoresist development waste and at least part of the photoresist-containing waste recovered from said recovery and refining unit, and at least one of pure or ultrapure water and tetraalkylammonium hydroxide through operation of the measured values of photoresist concentration and tetraalkylammonium hydroxide concentration as input data.
3. Equipment for recovering a developer from a photoresist development waste and reusing it as claimed in claim 1; wherein said rejuvenated developer adjustment unit is further provided with at least one of a pure or ultrapure water addition line and a tetraalkylammonium hydroxide addition line for replenishing said tetraalkylammonium hydroxide solution and at least one of part of the photoresist development waste and at least part of the photoresist-containing waste with at least one of pure or ultrapure water and tetraalkylammonium hydroxide.
4. Equipment for recovering a developer from a photoresist development waste and reusing it as claimed in claim 1; which further comprises at least one of a cation exchange resin treatment unit and a chelate resin treatment unit, or a cation exchange resin and chelate resin mixed bed treatment unit for treating said part of the photoresist development waste with said at least one of the cation exchange resin treatment unit and the chelate resin treatment unit, or said cation exchange resin and chelate resin mixed bed treatment unit.
5. Equipment for recovering a developer from a photoresist development waste and reusing it as claimed in claim 1; which further comprises at least one of a cation exchange resin treatment unit and a chelate resin treatment unit, or a cation exchange resin and chelate resin mixed bed treatment unit for treating said at least part of the photoresist-containing waste with said at least one of the cation exchange resin treatment unit and the chelate resin treatment unit, or said cation exchange resin and chelate resin mixed bed treatment unit.
6. Equipment for recovering a developer from a photoresist development waste

and reusing it; comprising a source of photoresist development waste including tetraalkylammonium hydroxide; a recovery and refining unit for separating impurities including photoresist from a photoresist development waste to recover tetraalkylammonium hydroxide solution, a first rejuvenated developer adjustment unit operable for replenishing the recovered tetraalkylammonium hydroxide solution with at least one of pure or ultrapure water and tetraalkylammonium hydroxide as needed to obtain a first rejuvenated developer having a desired tetraalkylammonium hydroxide concentration, a second rejuvenated developer adjustment unit operable for replenishing at least one of part of the photoresist development waste and at least part of a photoresist-containing waste recovered from said recovery and refining unit with at least one of pure or ultrapure water and tetraalkylammonium hydroxide as needed to obtain a second rejuvenated developer having a desired tetraalkylammonium hydroxide concentration, a mixer for mixing the first rejuvenated developer with the second rejuvenated developer to prepare a mixed rejuvenated developer, and a development unit arranged to be fed with said mixed rejuvenated developer.

7. Equipment for recovering a developer from a photoresist development waste and reusing it as claimed in claim 6; which further comprises flow meters for measuring the respective flow rates of the first rejuvenated developer and the second rejuvenated developer, a photoresist concentration determination apparatus for the second rejuvenated developer, a photoresist concentration determination apparatus for the mixed rejuvenated developer, and a controller for controlling the respective flow rates of the first rejuvenated developer and the second rejuvenated developer in such a manner that the photoresist concentration of the mixed rejuvenated developer becomes a desired value through operation of the measured values of flow rates and photoresist concentrations as input data.

8. Equipment for recovering a developer from a photoresist development waste and reusing it as claimed in claim 6; which further comprises at least one of a cation exchange resin treatment unit and a chelate resin treatment unit, or a cation exchange resin and chelate resin mixed bed treatment unit for treating said part of the photoresist development waste with said at least one of the cation exchange resin treatment unit and the chelate resin treatment unit, or said cation exchange resin and chelate resin mixed bed treatment unit.

9. Equipment for recovering a developer from a photoresist development waste and reusing it as claimed in claim 6; which further comprises at least one of a cation exchange resin treatment unit and a chelate resin treatment unit, or a cation exchange resin and chelate resin mixed bed treatment unit for treating said at least part of the photoresist-containing waste with said at least one of the cation exchange resin treatment unit and the chelate resin treatment unit, or said cation exchange resin and chelate resin mixed bed treatment unit.

10. Equipment for recovering a developer from a photoresist development waste and reusing it; comprising a source of photoresist development waste including tetraalkylammonium hydroxide; a rejuvenated developer adjustment unit comprising a development waste storage and rejuvenated developer adjustment tank, a recovery and refining unit operable for separating impurities including photoresist from a solution sent from said development waste storage and rejuvenated developer adjustment tank to recover a tetraalkylammonium hydroxide solution, means for returning said recovered solution to said development waste storage and rejuvenated developer adjustment tank and mixing it with the solution in said development waste storage and rejuvenated developer adjustment tank to prepare a rejuvenated developer, and a

development unit arranged to be fed with said rejuvenated developer.

11. Equipment for recovering a developer from a photoresist development waste and reusing it as claimed in claim 10; which further comprises a circulation line attached to said rejuvenated developer adjustment unit and provided with a photoresist concentration determination apparatus for the solution in said development waste storage and rejuvenated developer adjustment tank and a tetraalkylammonium hydroxide concentration determination apparatus for the solution in said development waste storage and rejuvenated developer adjustment tank, and a controller for controlling to desired values the respective flow rates of at least part of the photoresist development waste and the tetraalkylammonium hydroxide solution through operation of the measured values of photoresist concentration and tetraalkylammonium hydroxide concentration as input data.
12. Equipment for recovering a developer from a photoresist development waste and reusing it as claimed in claim 10; which further comprises at least one of a pure or ultrapure water addition line and a tetraalkylammonium hydroxide addition line for replenishing the recovered tetraalkylammonium hydroxide solution with at least one of pure or ultrapure water and tetraalkylammonium hydroxide as needed.
13. Equipment for recovering a developer from a photoresist development waste and reusing it as claimed in claim 12; wherein said controller is further used for controlling to a desired value the flow rate of at least one of pure or ultrapure water and tetraalkylammonium hydroxide, said flow rate being controlled before said development waste storage and rejuvenated developer adjustment tank.
14. Equipment for recovering a developer from a photoresist development waste and reusing it as claimed in claim 10; which further comprises a photoresist-containing waste recovery line for recovering a photoresist-containing waste from said recovery and refining unit and returning back at least part of said photoresist-containing waste to said development waste storage and rejuvenated developer adjustment tank.
15. Equipment for recovering a developer from a photoresist development waste and reusing it as claimed in claim 14; wherein said controller is further used for controlling to a desired value the flow rate of at least part of the photoresist-containing waste recovered from said recovery and refining unit, said flow rate being controlled before said development waste storage and rejuvenated developer adjustment tank.
16. Equipment for recovering a developer from a photoresist development waste and reusing it as claimed in claim 14; which further comprises at least one of a cation exchange resin treatment unit and a chelate resin treatment unit, or a cation exchange resin and chelate resin mixed bed treatment unit for treating said at least part of the photoresist-containing waste with said at least one of the cation exchange resin treatment unit and the chelate resin treatment unit, or said cation exchange resin and chelate resin mixed bed treatment unit.

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L7: Entry 5 of 36

File: USPT

Oct 21, 2003

DOCUMENT-IDENTIFIER: US 6635177 B2

TITLE: Reclaiming water and usable brine concentrate from domestic sewage

Brief Summary Text (10):

According to one embodiment of the invention, the treatment and reclamation process includes an intensely anaerobic methane producing process followed by a highly aerobic algal-based waste oxidation process, a Dissolved Air Flotation (DAF) process, a Slow Sand Filtration (SSF) and/or other filtration process (e.g., microfiltration, nanofiltration, ultrafiltration, etc.), a disinfection process and finally a Reverse Osmosis (RO) process. The anaerobic process precipitates most heavy metals as metal sulfides, and the aerobic algal-based wastewater treatment process entails the use of algae to adsorb the remaining heavy metals. The DAF process removes suspended solids and algae from the treated sewage. The SSF process ensures that substantially all suspended solids and microorganisms are removed from the treated sewage. The disinfection process eliminates microorganisms that are not already filtered out. Finally, the reverse osmosis process removes the remaining dissolved solids from the treated sewage to produce permeate water and a high salinity concentrate (e.g., brine). The permeate water is potable and the high salinity concentrate is substantially free of heavy metal ions. Preferably, the high salinity concentrate is used to cultivate halophilic algae, such as *Dunaliella*, which have a high commercial value. Thus the present invention provides for a method of reclaiming both water and high salinity concentrate from sewage. The present invention can also be used to reclaim other types of wastewater.

Detailed Description Text (11):

According to the present embodiment, the water in the maturation pond 120 is further subjected treatment by two Slow Sand Filtration units 122 (and/or other filtration units such as microfiltration units, nanofiltration units, ultrafiltration units, etc). In one implementation, the SSF units 122 are constructed from two 3.05-m diameter, 2.1-m deep cross-linked polyethylene tanks, filled to a depth of one meter with filtration media. The base gravel layer was 30 cm of 1.9- to 1.25-cm round gravel topped by a 25-cm layer of pea gravel. These gravel layers covered a network of 7.5-cm diameter corrugated ABS perforated drain pipe. The gravel layers were then covered with a 46-cm layer of 30-mesh, silica, water filter sand. After 180 hours of system operation, layers of geotextile fabric were installed on top of the sand. This fabric, which may increase the interval between filter cleanings, is preferably Amoco Style 4512, a nonwoven polypropylene felted geotextile. The fabric is 3.3 mm thick and has a specific surface area of 16,424 m²/m² and a porosity of 85%. Both sand filters were operated with a covering of between one and seven layers of fabric for the remainder of the test period. The SSF units 122 are operated in parallel at a total flow rate of nineteen liters per minute. A constant water depth of two meters (measured from the bottom of the tank) should be maintained in the SSFs. When the combined flow through the filters dropped below nineteen liters per minute, the filters may require cleaning. Filter cleaning intervals may range from five and ten days.

Detailed Description Text (15):

With reference still to FIG. 1, the RO unit 126 has a 1-1 membrane vessel configuration with three membrane elements in each membrane vessel. The elements are preferably Koch/Fluid Systems 4820HR Spiral Wound Thin Film Composite

membranes. The membranes are operated at a feed pressure of 9 to 11 bar. RO membrane fouling rate is calculated from measurements taken by flow and pressure instruments on the RO skid. The water permeation coefficient, A_w , can be calculated using the NORMPRO software provided by Koch/Fluid Systems.

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